

THE KINETICS OF ELEMENTARY REACTIONS

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by

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The fundamental aim of the work contained in this thesis is the better understanding of the factors that govern the rates of chemical reactions. Most of the work is concerned with the investigation of reactions in the gas phase, because homogeneous gas reactions may be expected to yield most readily to theoretical treatment. True gas reactions are free from such complicating factors as solvation, adsorption and, except in special cases, diffusion. There are however some solution reactions which might be simple; they are the reactions for which the transfer of a proton is the rate-determining step. Some of the work in this thesis is concerned with reactions of this type. It will be seen from the published papers that the most complex experimental techniques are often required to investigate the reactions of greatest formal simplicity. The rate constants of these simple reactions can usually only be measured when the experimental systems are carefully designed for this specific purpose.

The whole subject of the kinetics of elementary gas reactions has been surveyed in the writer's monograph 'Gas Kinetics'. This monograph is a critical account of all the literature on the subject that was available to the writer in July 1954. The investigations that were selected for discussion were chosen because they throw light on the problem of why reactions occur at the rate they do. The book

defines the attitude that has governed the writers approach to the subject of this thesis. Publication (14) contains a short summary of the present position in the subject. The relevance of modern work to elementary teaching has also been discussed (15).

A fruitful approach to the understanding of the pre-exponential factors of elementary reactions lies in the consideration of the entropy changes involved. This approach has been discussed in general terms (2) for the major classes of gas reactions and specifically for the reactions of chlorine atoms (12) and methylene (22). Particular attention has been paid to the combination of free radicals. It has been shown that the reverse decompositions of normal molecules into radicals have remarkably pre-exponential factors; they are in several cases greater than $10^{15} \text{ sec.}^{-1}$.

Unimolecular decompositions and the opposing combination reactions are among the simplest of all chemical processes. Our knowledge of them is more complete than it is for any other class of gas reaction. A problem on which much work still remains to be done is the elucidation of the conditions under which the rate of transfer of energy determines the rates of unimolecular reactions. Publications (3) and (4) bear directly on this point. The isomerization of cyclopropane has proved amenable to theoretical treatment and has provided the best test so far of N.B.Slater's theory

of unimolecular reactions. The efficiency with which energy is transferred between molecules on collision is of great importance in connection with all such theoretical treatments. The work on the effect of added gases on the rates of the isomerization of cyclopropane (3) and the decomposition of cyclobutane (4) provides the first evidence that all complex molecules probably have unit efficiency in the transfer of energy on collision. This only applies to molecules that are chemically activated; the efficiency of transfer is much lower for molecules containing less energy. Two unsuccessful attempts to extend the present knowledge of the phenomena of energy transfer are recorded in publications (23) and (24).

The study of the thermal decomposition of azomethane (5) played an important part in the development of modern ideas on energy transfer. Some aspects of the decomposition, as described in the early papers appeared unusual in the light of modern knowledge. A fresh investigation was therefore undertaken using a flow system; however it seems that all the problems are not yet solved. The writer is presently engaged in further work on this topic.

The activation energies for the unimolecular decomposition of molecules into radicals are closely equal to the strengths of the bonds broken. The fact that a knowledge of these bond strengths is necessary for a proper understanding of radical reactions has been a great stimulus to the investigation of the decompositions. The strengths of the methyl-carbon bonds

in dimethyl mercury, dimethyl cadmium, dimethyl zinc and methyl zinc (25,26) have been determined in this way. These results are the first fruits of a projected survey of the strengths of the bonds between methyl groups and many metals. The probable values of the dissociation energies of the C-C bonds in cyclanes have been discussed with reference to the mode of unimolecular decomposition (18,19). The strength of the $\text{CF}_3\text{-H}$ bond has also been determined (21) and hence the heat of formation of the trifluoromethyl radical has been found.

Another class of thermal decompositions is that of the molecular eliminations, in which a molecule splits into two normal molecules in one step without the intervention of free radicals. Little is as yet known of the factors which control the rates and activation energies of these reactions. At the moment the principal need seems to be for the investigation of more classes of compounds. The decomposition of cyclobutane is a reaction of this type. Similar reactions which have been studied by the writer are the decompositions of cyclopentyl bromide (11) into cyclopentene and hydrogen bromide, the decomposition of *t*-butyl formate into formic acid and *iso*-butene⁽²⁹⁾ and the decomposition of *t*-butylamine (6). The last reaction is remarkable because two alternative sets of products corresponding to the elimination of methane and ammonia are formed in comparable quantities. The general

features of these reactions are considered in the writer's book and the discussion is brought up to date in the paper on t-butyl formate. It is shown that similar factors determine the relative rates of many series of reactions of this type.

The addition of methylene to alkanes (31) may be regarded as similar to these combination reactions which are the reverse of the molecular reactions that have just been discussed. No free radicals with only one unsatisfied valence are involved in either case. The study of the carbenes is just beginning, it promises to be a significant new field of radical chemistry.

A further class of simple reactions comprises those in which an atom is transferred from one radical group to another. They may be represented by the equation



where A and C are free radicals. The writer has examined three series of reactions of this type and measured their rate constants. The factors determining the magnitude of the pre-exponential terms in the Arrhenius equations for these reactions are fairly well understood. Greatest interest therefore attaches to the problem of the magnitude of the activation energies. The experimental approach to its solution lies in the measurement of these activation energies for a large number of members of as many different series

of reactions as possible.

The writer has been responsible for the extensive investigation of three classes of such reaction. They are the reactions of methyl radicals, of trifluoromethyl radicals, and of chlorine atoms with compounds containing hydrogen. In general they have been studied by competitive techniques (30) which offer many advantages.

The basic papers on the reactions of methyl were written by the writer under the direction of Dr Steacie and consequently do not form part of this thesis. However the early work is summarized and discussed in a review (1). The more recent work of the writer has been concerned with certain special problems. Thus the decomposition of di-t-butyl peroxide, which is generally an unsatisfactory source of the radicals, was used to investigate the reactions of thermal methyl radicals with ketones.⁽⁷⁾ This problem was of interest because the photolysis of ketones is frequently used as a source of free radicals. The reactions of methyl radicals with thiols have been studied (28) because these compounds are of importance as chain transfer reagents in polymerisations. They react very rapidly with free radicals. Indeed the reactions are too rapid for convenient estimation of their rates and the results have only semi-quantitative significance. The special case of the reaction of methyl with acetaldehyde has also been discussed (17).

The reactions of trifluoromethyl radicals have been

studied (10,20) using hexafluoroazomethane as the source of radicals. The results show that the trifluoro- radicals are more reactive than ordinary methyl radicals. The higher reactivity is reflected in activation energies which are 2 - 3 kcal./mole lower.

Chlorine atoms were found (12,16) to be much more reactive than ordinary polyatomic radicals. The pre-exponential factors approach the rate of collisions between the atoms and the substrates. Furthermore the activation energies are very low; often they are of the order of 1 kcal./mole.

Some information on the reactivity of thiyl radicals has been obtained from the study of the photo-initiated decomposition of acetaldehyde catalysed by thiols (23).

Our knowledge of transfer reactions will be very usefully increased when processes involving the transfer of atoms other than hydrogen have been investigated. An attempt to investigate the transfer reaction of iodine atoms with methyl iodide (8) was unsuccessful because of an excessive heterogeneous reaction.

The rate-determining step of an acid-base-catalysed reaction is generally the transfer of a proton between two molecules or ions. These reactions therefore bear a marked resemblance to the hydrogen transfer reactions that have just been discussed. Most work on acid-base catalysis has been performed in aqueous solutions. The properties of water are known to vary with temperature in an irregular

manner. Accordingly it is not surprising that little work has been done on the measurement of the activation energies of acid-base catalysed reactions. However it should be possible to obtain useful information by working in non-aqueous solvents. A start has been made by investigating the temperature dependence of the decomposition of nitramide in anisole catalysed by anilines (27). The results indicate a linear relation between the activation energies and the logarithms of the rate constants.

The crystal structure of nitramide was determined (13) both because it is good to know the structure of the substances with which one is working and it seemed that a knowledge of the structure would throw light on the nature of N-H-O hydrogen bonds. Unfortunately the hydrogen atoms could not be accurately located. The precision of the analysis was lower than had been hoped because a pronounced anisotropic heat motion was found.

The monograph on 'Gas Kinetics' is largely a critical survey of the literature, but the arrangement and treatment have not been attempted before. Much of the information lay scattered about the literature. The general significance of the experimental facts was not clear until they had been correlated. Much of the discussion in Chapter 5 is original.

Publications.

The remainder of this thesis consists of copies of the papers that have been referred to in the introduction. The writer was responsible for the general conception of the investigations. He designed the greater part of the apparatus, and did a considerable portion of the experimental work, especially in the construction of the equipment. He was the junior author of the publication on the crystal structure of nitramide; while investigating this problem he was learning the technique of X-ray crystallography from Dr.C.A.Beevers. The writer wishes to express his gratitude to his colleagues and students who have contributed so largely to the work recorded here.

Those papers which are in manuscript have been submitted for publication, either to the Chemical Society or the Faraday Society.

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Book.

Gas Kinetics: An Introduction to the Kinetics of

Homogeneous Gas Reactions.

Published Papers.

- R 1. The Reactions of Methyl Radicals.
2. Entropy Changes in Free Radical Reactions.
3. Studies in Energy Transfer II. The Isomerization of Cyclopropane -a quasi- Unimolecular Reaction.
4. Studies in Energy Transfer III. The Effect of Added Gases on the Decomposition of Cyclobutane.
5. The Thermal Decomposition of Azomethane.
6. The Thermal Decomposition of *t*-Butylamine.
7. The Reactions of Methyl Radicals with Acetone, Diethyl Ketone and Di-*t*-butyl Peroxide.
8. The Exchange of Iodine Atoms between Iodine and Methyl Iodide in the Temperature Range 150-375°.
9. The Study of Chlorine Atom Reactions in the Gas Phase.
- with H.O.Pritchard and J.B.Pyke.

31. The C-H Bond Dissociation Energy in Fluorofen.
10. The Reactions of Trifluoromethyl Radicals. Schiff.
22. with G.O.Pritchard, H.O.Pritchard and H.I.Schiff.
11. The Thermal Decomposition of Cyclopentyl Bromide.
23. with S.J.W.Price and R.Shaw. *same at very low*
12. The Reactions of Chlorine Atoms - A Test of the
Transition State Theory. G.Sowden.
24. with J.H.Knox. *of Nitrogen Atoms.*
13. The Crystal Structure of Nitramide, NH_2NO_2 .

Papers with C.A.Beevers. publication.

- R 14. Recent Developments of Gas Kinetics. *of Dimethyl*
General. *reury and Dimethyl Cadmium.*

- R 15. The Teaching of Chemical Kinetics.

Shorter Contributions. *ads 2. The Pyrolysis of Dimethyl*

16. A Method for the Study of Chlorine Atom Reaction.
The Reaction $\text{Cl} - \text{CH}_4 \rightarrow \text{CH}_3 - \text{HCl}$.
27. with H.O.Pritchard and J.B.Pyke. *Anisole Catalys-*
17. The Photolysis of Acetaldehyde.
with G.O.Pritchard and H.O.Pritchard. *J.B.Slater*
18. The C-C Bond Dissociation Energies in Cyclanes.
28. with H.O.Pritchard. *Decomposition of Acetaldehyde*
19. The C-C Bond Dissociation Energy in Cyclobutane.
with H.O.Pritchard. *F.Smith and H.Wilkie.*
20. The Photolysis of Hexafluoroazomethane and the
Reactions of CF_3 Radicals with Methane and n-
Butane.
with G.O.Pritchard, and H.O.Pritchard.

21. The C-H Bond Dissociation Energy in Fluorofom.
with G.O.Pritchard, H.O.Pritchard and H.I.Schiff.
22. The Reactions of Methylene.
with J.H.Knox.
23. The Isomerization of Cyclopropane at very low Pressures.
with J.H.Knox.
24. The Combination of Nitrogen Atoms.
with G.Boocock and H.O.Pritchard.

Papers in the course of publication.

25. Carbon-Metal Bonds I. The Pyrolyses of Dimethyl Mercury and Dimethyl Cadmium.
with S.J.W.Price.
26. Carbon Metal Bonds 2. The Pyrolysis of Dimethyl Zinc.
with S.J.W.Price.
27. The Decomposition of Nitramide in Anisole Catalysed by Anilines.
with G.C.Fettes, J.A.Kerr, A.McClure, J.S.Slater and C.Steel.
28. The Photoinitiated Decomposition of Acetaldehyde Catalysed by Thiols.
with R.N.Birrell, R.F.Smith and H.Wilkie.
29. The Pyrolysis of t-Butyl Formate.
with R.Gordon and S.J.W.Price.

30. The Study of Free Radical Reaction by Competitive methods.

with J.H.Knox.

L 31. The Reactions of Methylene with Alkanes, with J.H.Knox.

✓ 32. The Reactions of Methyl Radicals with Thiols. with J.A.Kerr.

THE REACTIONS OF METHYL RADICALS

BY
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THE REACTIONS OF METHYL RADICALS

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A LARGE proportion of contemporary research on reaction kinetics is devoted to the study of atomic and free-radical reactions both in the gas phase and in solution. There are many reasons for this. First, atomic and free-radical reactions are formally very simple; they are less influenced by their environment than are ionic reactions; they exemplify clearly the factors governing reactivity; they are often very symmetrical and are suitable for theoretical study; they may provide the avenue by which we shall arrive at a fuller understanding of the factors influencing the rates of reactions. Secondly, they are of extreme practical importance in the petroleum chemicals industry and in the production of high polymers. Thirdly, they are involved in many combustion and oxidation processes. Fourthly, they are relatively difficult to investigate and their study involves the use of many of the most advanced chemical techniques, so they provide a challenge to the worker in reaction kinetics.

Here we shall be concerned with the reactions of methyl radicals in the gas phase, which have been more fully investigated and are better understood than those of any other free radicals. As a result of intensive research in five or six laboratories during the last seven years we now have some quantitative knowledge of most types of methyl-radical reaction. Consequently, it is possible to write a fairly comprehensive review of these reactions in the expectation that new work will amplify what is written here and fill in the many gaps but that drastic revision will not be required. Here will be described the methods of research used in the study of methyl-radical reactions and the results so obtained, in the hope that this particular account may be a general guide to free-radical research in the gas phase. To this end the parallel behaviour of other radicals, which are much more difficult to investigate, will be referred to when this seems to be illuminating.

Early Work on Free Radicals.—The existence of short-lived alkyl free radicals was first demonstrated twenty years ago by Paneth and his co-workers. In the subsequent decade investigators were primarily concerned in detecting the presence of free radicals in reacting systems. Paneth showed that when organic vapours were passed through a furnace at a convenient temperature and over a metallic mirror, the mirror was removed and metallic alkyls were formed; by this means it was shown that aliphatic free radicals were intermediates in a large number of pyrolyses and photolyses. Two other methods were developed to accomplish this end. Hinshelwood showed in 1936 that the addition of very small quantities of nitric oxide to the reacting system greatly inhibited the pyrolysis of many organic vapours. Nitric oxide is a molecule containing an odd number of electrons and it was expected that it would combine very rapidly with free radical

to give a compound with the usual even number of electrons. Since the free-radical chain-carriers in a pyrolysis are present in very small concentrations (often of the order of 10^{-10} mole per l.), a very small quantity of nitric oxide should greatly inhibit the overall reactions. Hinshelwood also showed that propene in larger quantities had a similar effect. Hence reactions which are inhibited by nitric oxide and propene probably involve free radicals. Patat and Sachsse showed that the reacting mixtures in pyrolyses would accelerate the ortho-para-hydrogen conversion, as would be expected if free radicals were involved. All of these techniques and their applications to particular systems are described fully in Steacie's definitive monograph.¹

The theory needed to explain many of these observations was provided by Rice and Herzfeld, who showed that the experimental data on pyrolysis reactions *could* be interpreted on the basis of free-radical mechanisms involving several simple elementary processes about which reasonable assumptions could be made. At that time no particular mechanism could be rigorously tested because not enough was known about the elementary reactions. Even today our knowledge of some of the postulated steps is inadequate for unequivocal judgments of the mechanisms favoured by Rice. However, it has been shown that Rice's anticipation was often remarkably accurate. Steacie¹ gives very complete accounts of these mechanisms.

Modern Developments.—During the last decade the interest of most investigators has shifted from the qualitative study of complex systems to the quantitative study of the elementary processes occurring in pyrolyses, photolyses, and polymerisations. In order to avoid complicating side reactions, these reactions are normally carried to very low percentage conversions and in consequence the analytical problems are great. The researches have been made possible by advances in analytical technique and by the increasing availability of isotopic tracers. The important analytical techniques which were mostly developed for oil companies in the United States are low-temperature distillation, Blacet and Leighton's analysis system,² and the analytical mass-spectrometer; as yet, the recording infra-red spectrometer has been comparatively little used in the study of free-radical reactions. As examples of the power of these methods it may be mentioned that by low-temperature distillation it is now possible to estimate 0.1 ml. (S.T.P.) of ethane in the presence of 15 ml. of propane to an accuracy of $\pm 3\%$ in $1\frac{1}{2}$ hours. The proportion of ethylene in an ethylene-ethane sample of 20 μ l. may be determined in 40 minutes to an accuracy of $\pm 0.05 \mu$ l. with Blacet and Leighton's apparatus. Under favourable conditions the proportion of CD_3H in CD_4 may be determined in 15 minutes to better than 0.1% on a mass-spectrometer. These are powerful new tools for the investigation of gas-reactions.

The Types of Methyl-radical Reaction.—There are three principal classes of methyl-radical reaction:

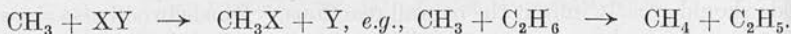
1. *Combination reactions*: $\text{CH}_3 + \text{XY} \rightarrow \text{CH}_3\text{XY}$, e.g., $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$. Methyl radicals will combine with methyl radicals, other free

¹ "Atomic and Free Radical Reactions", Reinhold, New York, 1947.

² *Ind. Eng. Chem. Anal.*, 1931, **3**, 266.

radicals, atoms, or "odd electron" molecules to give normal saturated molecules.

2. Metathetical reactions:



Methyl radicals will extract atoms from molecules to produce saturated methyl derivatives and a new free radical or atom. This class of methyl radical reaction has been intensively studied, especially those reactions in which a hydrogen atom is extracted. At least two cases of the extraction of a radical from a molecule are known, namely, that of acetyl from diacetyl and that of methyl from dimethylmercury.

3. *Addition reactions*: $\text{CH}_3 + \text{XY} \rightarrow \text{CH}_3\text{XY}$, e.g., $\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_7$. Methyl radicals will add to molecules containing multiple bonds to give more complex free radicals.

Only these three types of methyl-radical reaction have been established beyond reasonable doubt. All the more complex alkyl radicals can undergo the following two other sorts of reaction which make the study of their behaviour very difficult.

4. *Decomposition reactions*: e.g., $\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$. That decomposition reactions of this type occur has been established, but very few have been studied quantitatively because there are few suitable radical sources. Mercury photosensitisation has so far proved to be the best source, and the decomposition of the radicals derived from the abstraction of a hydrogen atom from ethane,³ propane,⁴ *n*-butane, 2-methylpropane,⁵ methyl alcohol,⁶ and dimethyl ether⁷ has been studied in this way. The reaction $\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$ is theoretically possible but probably has an activation energy of at least 80 kcal. and will not become appreciable until temperatures of 1000° K are reached. By contrast, the decomposition of the *n*-butyl radical can be detected at 500° K.

5. *Disproportionation reactions*: e.g., $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$. Very little is known about reactions of this type, but they certainly occur under some conditions, for Ivin and Steacie⁸ have accurately studied the disproportionation of ethyl radicals in the photolysis of diethylmercury. The only evidence for the reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2$ comes from the work of Bawn and Tipping⁹ which appears to be quite unrelated to normal work on homogeneous gas-phase reactions, probably because the reaction was studied in an atmosphere of sodium vapour.

From this list we can see that all known reactions of methyl radicals are bimolecular at high pressures. Consequently, the reactions may be



³ Bywater and Steacie, *J. Chem. Physics*, 1951, **19**, 172.

⁴ *Idem, ibid.*, p. 319.

⁵ *Idem, ibid.*, p. 326.

⁶ Phibbs and Darwent, *ibid.*, 1950, **18**, 495.

⁷ Marcus, Darwent, and Steacie, *ibid.*, 1948, **16**, 987.

⁸ *Proc. Roy. Soc.*, 1951, **A**, **208**, 25.

⁹ *Discuss. Faraday Soc.*, 1947, **2**, 104.

represented by equation (a) or (b). In these two cases the respective rate constants k_a and k_b are defined by the equations

$$R_b \equiv d[B]/dt = -d[A]/dt = k_a[CH_3][A]$$

and
$$R_y \equiv d[Y]/dt = R_z \equiv d[Z]/dt = -d[X]/dt = k_b[CH_3][X]$$

where the letters in brackets are the concentrations of the substances and R_y is the rate of formation of Y, and so on: this notation will be used throughout. Hence if the methyl-radical concentration is known, the rate constant in the first case can be found by measuring the formation of B or the disappearance of A, and in the second case by the disappearance of X or the formation of Y or Z.

The rate constants all obey the Arrhenius equation $k = A \exp(-E/RT)$ within the limits of experimental error, where E is the activation energy of the reaction and A , which is usually called the pre-exponential or A factor, is a number having the dimensions of a rate constant. The Arrhenius equation may be written in terms of the collision theory of chemical kinetics for a bimolecular reaction as $k = PZ \exp(-E/RT)$, where P is known as the steric factor, and Z , the collision frequency of the reacting species, is given by

$$Z = \sigma_{x,y}^2 \left[8\pi kT \frac{(m_x + m_y)}{m_x m_y} \right]^{\frac{1}{2}}$$

where $\sigma_{x,y}$ is the mean molecular (collision) diameter of X and Y; m_x and m_y are the masses of the respective molecules, and k is Boltzmann's constant.

The great value of the collision theory is that it provides a very simple picture of chemical kinetics, as a large number of reactions is known in which $P = 1$. A weakness is that Z is not a well-defined quantity, because of the uncertainty as to the appropriate values for the collision diameters. To preserve the simplicity of the theory, collision diameters which might be determined by viscosity and other methods depending on the transport properties of the gases should be selected. Almost all workers on methyl radicals have done this when calculating steric factors, but despite the uniformity of practice it is probably less likely to cause confusion if the directly determinable A factors are given. Throughout this Review, A factors will be quoted but for purposes of comparison and as an *aide-memoire* the two following values of Z are given:

Z for the collision of two methyl radicals at 455°K with collision diameters of $3.5 \text{ \AA} = 2 \times 10^{-10} \text{ molecules}^{-1} \text{ c.c. sec.}^{-1} = 1 \times 10^{14} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$.

Z for the collision of a methyl radical at 455°K with a molecule of molecular weight 50 and a collision diameter of $5.5 \text{ \AA} = 6 \times 10^{-10} \text{ molecules}^{-1} \text{ c.c. sec.}^{-1} = 4 \times 10^{14} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$.

There are two principal difficulties which must now be considered in the study of methyl radicals: first, a suitable source of them must be selected, and secondly, some way of determining the steady state concentration of methyl radicals, usually about $10^{-12} \text{ mole/c.c.}$, must be found.

Sources of Methyl Radicals.—Hitherto the methyl radicals required for

of the type $M + h\nu = nA$, $A + B = X$, and $2A = Y$, so that the rate of formation of one product is dependent upon the first power of the concentration of A and the rate of formation of the second is dependent upon the second power of this concentration, it is possible to use the method of intermittent illumination to find the two rate constants involved. In two recent articles¹⁵ reference has been made to the application of the method of intermittent illumination to the determination of absolute rate constants in polymerisation and liquid-phase oxidation reactions. A full description of the mathematical theory of the method has been given by Burnett and Melville.¹⁶ A "pilot" reaction of the type $A + B = X$ is used to measure the average concentration of the transient radical A during the run, for if B is in excess the average concentration of A is directly proportional to the rate of production of X. However, while sufficient quantities of X must be obtained for accurate analysis it is essential that the concentration of A in the system should not be appreciably disturbed owing to formation of X. In the polymerisations and oxidations this difficulty does not arise because the over-all chain process may be used as the "pilot" reaction, in which a new radical is formed each time the radical A reacts with B; but for the study of methyl-radical reactions, high light intensities and low temperatures must be used, so the amount of methyl reacting with B is a negligible (*ca.* 0.5%) part of the total amount of methyl released in the system. All the accurate absolute rate constants of methyl-radical reactions are based upon rotating sector determinations of the rate of methyl-radical combination.

When a mixture of acetone and another hydrogen-containing compound



is photolysed the reaction (1) will take place as well as reactions (2) and (3). Now

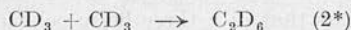
$$R_{\text{CH}_4} = k_3[\text{CH}_3][\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3] + k_1[\text{CH}_3][\text{RH}]$$

and

$$R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6} = k_3[\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3]/k_2^{\frac{1}{2}} + k_1[\text{RH}]/k_2^{\frac{1}{2}}$$

But the term $k_3[\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3]/k_2^{\frac{1}{2}}$ has already been determined, so $k_1/k_2^{\frac{1}{2}}$ and consequently $E_1 - \frac{1}{2}E_2$ and $A_1/A_2^{\frac{1}{2}}$ can be found. All the results listed in Tables 3 and 4, for which the radical source was acetone or dimethyl-mercury, were obtained in this way.

An alternative procedure is to use fully-deuterated acetone, for which $k_3^*/k_2^{*\frac{1}{2}}$ may be obtained as before for reactions (3*) and (2*):



In the presence of a hydrogen-containing compound, reaction (1*) occurs:



Hence

$$k_1^*/k_3^* = R_{\text{CD}_3\text{H}}[\text{CD}_3\cdot\text{CO}\cdot\text{CH}_3]/R_{\text{CD}_4}[\text{RH}]$$

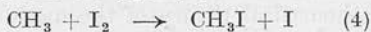
The ratio $R_{\text{CD}_3\text{H}}/R_{\text{CD}_4}$ can be rapidly and accurately determined, so k_1^*/k_3^*

¹⁵ Bolland, *Quart. Reviews*, 1949, **3**, 1; Burnett, *ibid.*, 1950, **4**, 292.

¹⁶ *Proc. Roy. Soc.*, 1947, *A*, **189**, 456.

can be found. Since the relation between k_3^* and k_3 has been determined, this is a method of finding k_1 . All the results listed in Tables 3 and 4, for which the radical source was hexadeuteroacetone, were obtained in this way.

An extension of this principle is involved in the method which has been used for the study of very fast methyl reactions. If the number of methyl radicals produced in a system is known, and there are only two methods by which the radicals can disappear, such as reactions (4) and (5)



then

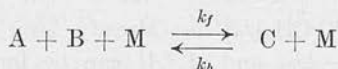
$$R_{\text{CH}_4} = k_5[\text{CH}_3][\text{HI}]$$

$$R_{\text{CH}_3\text{I}} = \text{Rate of methyl production} - R_{\text{CH}_4} = k_4[\text{CH}_3][\text{I}_2]$$

$$\text{Therefore } k_5/k_4 = \frac{R_{\text{CH}_4}[\text{I}_2]}{[\text{Rate of methyl production} - R_{\text{CH}_4}][\text{HI}]}$$

Unfortunately, k_4 has not yet been determined absolutely, so only relative constants are obtained by this method.

The Combination Reactions of Methyl Radicals.—Because the methyl radical contains only four atoms, one of them heavy and three light, there is a possibility that the rate of methyl-radical combination with other small radicals and atoms will be markedly dependent on the pressure in the system in which the reaction is studied owing to third-body effects. This phenomenon is the exact converse of that observed in those unimolecular decomposition reactions the rate of which falls off at low pressures, and is similar to the third-body effect observed in the combination of hydrogen, bromine, and iodine atoms. Lindemann, O. K. Rice, Ramsperger, and Kassel¹⁸ have developed the basic quantitative treatment of these "quasi-unimolecular" reactions. It is usually convenient when dealing with combination reactions to make use of the relation $k_f/k_b = K$, where the rate and equilibrium constants refer to the reactions



The problem of the combination of $\text{A} + \text{B}$ in the presence of a third body can then be "inverted" so as to be the problem of the decomposition of C in the presence of a neutral gas. Thus stated, the problem is more tractable for a number of reasons including the fact that the definition of a two-body collision is clear-cut whereas that of a three-body collision is not. Marcus and Rice¹⁹ recently considered the effect of pressure in the combination of methyl radicals with other methyl radicals and with iodine atoms. They concluded that energy-transfer effects should become important in the region of a few millimetres' pressure for the combination of methyl radicals

¹⁷ *J. Chem. Physics*, 1951, **19**, 85.

¹⁸ See L. S. Kassel, "Kinetics of Homogeneous Gas Reactions", Chemical Catalog Co., New York, 1932.

¹⁹ *J. Phys. Colloid Chem.*, 1951, **55**, 894; see also Marcus, *J. Chem. Physics*, 1952, **20**, 359.

and at pressures of hundreds of millimetres for the combination of methyl with an iodine atom.

The most important combination reaction of methyl radicals is that in which two of them combine to give ethane. This reaction has been very accurately studied by Gomer and Kistiakowsky,¹⁷ who used the photolysis of both acetone and dimethylmercury as radical sources, the total pressure in the reaction system being 10–50 mm. Using the rotating sector technique, they found the rate constants given in Table 1, where k_2 is in mole⁻¹ c.c. sec.⁻¹. From these figures it may be seen that the activation

TABLE 1. *Rate constants for the combination of methyl radicals*

Radical source	Temp.	$k_2 \times 10^{-13}$	Radical source	Temp.	$k_2 \times 10^{-13}$
Acetone	125°	4.5	Dimethylmercury .	175°	4.6
Acetone	175	4.2	Dimethylmercury .	220	6.7

energy of the reaction is very low and that the collision yield for the reaction is about 0.5. This work seems to be very reliable, and the results obtained will be used throughout this Review for the calculation of rate constants based on the rate of formation of ethane in systems at relatively high pressures. In fact, most methyl-radical reactions have been investigated in systems at pressures of 50–100 mm. where the rate constant for the combination reaction is almost independent of pressure. The first attempts to detect the falling-off of the rate constant for methyl combination were not conclusive,²⁰ largely because experimental errors and complications increased markedly as the pressure was lowered so that it was difficult to be sure that the observed trend was not fortuitous. However, Kistiakowsky and Kirk Roberts²¹ have now found that the rate constant for the combination of methyl radicals definitely falls to about one-third of its high-pressure value when the total pressure in the system is reduced to 1 mm. This is in good agreement with Marcus's prediction.¹⁹

Lossing, Tickner, and Ingold have also measured the rate of combination of methyl radicals by a mass-spectrometric method²² by which it is possible to observe directly the concentration of methyl radicals and ethane in a flow-reaction vessel attached to the ionisation chamber of the mass-spectrometer. Di-*tert.*-butyl peroxide, dimethylmercury, and ethylene oxide at a few microns' pressure in the presence of 5–19 mm. of helium as a carrier gas have been used as radical sources. The rate constant found at 160° c agrees within 50% with those of Gomer and Kistiakowsky at high pressures. The rate constant decreases with increasing temperature according to the equation $k \propto \exp[(2200 \pm 500)/RT]$ over the range from 160° to 800° c.

²⁰ Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1950, **19**, 1097; Nicholson *J. Amer. Chem. Soc.*, 1951, **73**, 3981; Linnell and W. A. Noyes, junr., *ibid.*, p. 3986.

²¹ Personal communication.

²² Lossing and Tickner, *J. Chem. Physics*, 1952, **20**, 907; Lossing, K. U. Ingold, and Tickner, *Discuss. Faraday Soc.*, 1953, **14**; also personal communication from Dr. Lossing.

Surprisingly, no evidence was found for the variation of rate with helium pressure.

The only other combination reaction which has been quantitatively studied is that of methyl with nitric oxide. The products of the reaction (6) are not known with certainty and are complex. Formaldoxime, ammonia,



hydrogen cyanide, and carbon monoxide have all been detected, so it is likely that a single molecule, perhaps $\text{CH}_3\cdot\text{NO}$, is first formed, which is unstable under the conditions of the experiment and rearranges or decomposes to give the observed products. The reaction has been studied by two methods, the first for the pressure range 5–100 mm. and the second for the range around 0.2 mm. Since the complex formed as a result of the reaction contains only six atoms, it would not be surprising if this rate constant were also dependent upon pressure, and this appears to be the case.

In the first method²³ the reaction is studied by photolysing acetone or dimethylmercury in the presence of nitric oxide at room temperature. A very low concentration of nitric oxide is kept constant by steadily leaking a known quantity of the gas into the reaction vessel during the run. After a convenient time (t) the reaction mixture was analysed for ethane and nitric oxide. Now

$$[\text{C}_2\text{H}_6] = tk_2[\text{CH}_3]^2$$

and

$$\text{total NO consumed} = tk_6[\text{CH}_3][\text{NO}]$$

The amount of nitric oxide found on analysis may be regarded as the steady-state concentration, for some 200 times this amount is added during the course of the run. From these equations and the accepted value of k_2 , k_6 is found to be $2 \times 10^{11} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$ at 28°C over the whole range of pressure.

The second method, first used by Forsyth,²⁴ has been greatly improved by Durham and Steacie,²⁵ who produced the methyl radicals by passing a stream of di-*tert*.-butyl peroxide through a furnace and down a tube into which nitric oxide could be injected. The concentration of methyl radicals at any point in the tube could be measured by following the rate of removal of a radioactive tellurium mirror. In this way the effect of the pressure of nitric oxide on the radical concentration along the reaction tube could be found, and hence the rate constant for the reaction of the radicals with nitric oxide. The value of $k_6 = 3.3 \times 10^{10} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$ at 25°C is much lower than the high-pressure value, but as there is no reason to suspect the experimental accuracy of either determination, this difference must be ascribed to the pressure dependence of the rate constant. Unfortunately, insufficient is known about the products of reaction (6) for the phenomenon to be treated theoretically.

A mass-spectrometer can also be used for methyl-radical detection,²²

²³ Marcus and Steacie, *Z. Naturforsch.*, 1949, **4**, a, 332; Miller and Steacie, *J. Chem. Physics*, 1951, **19**, 73.

²⁴ Forsyth, *Trans. Faraday Soc.*, 1941, **37**, 312.

²⁵ *J. Chem. Physics*, 1952, **20**, 582.

and in this way the rate constant was found to be 10^{11} mole $^{-1}$ c.c. sec. $^{-1}$ at 950° c, with rather a large experimental error; however, this figure may be taken as good evidence that the activation energy of the reaction is very small indeed.

It is generally believed that a large number of combinations of methyl radicals with other radicals occur, but only in a few cases have the products been identified, because of the analytical difficulties involved in the separation of small quantities of $R\cdot CH_3$ from large quantities of RH , where R is a large radical. However, the products of the combination of methyl with acetyl, acetonyl, *n*-propyl, and isopropyl have all been found, though none of the rate constants has been measured. Ivin and Steacie⁸ have found that ethyl radicals combine on about one collision in two to give butane, so it is very probable that the reactions of methyl with ethyl and of methyl with propyl have similar collision yields. These combinations of methyl with large radicals may be regarded as independent of pressure under all accessible conditions. The combination of methyl with a benzyl radical, reaction (7), has not been detected but there is no reason to suppose that it



does not occur. The activation energy for the decomposition of ethylbenzene as measured by Szwarc²⁶ may be combined with the C-H bond strengths in toluene and methane and the heats of formation of toluene, methane, and ethylbenzene to give the activation energy of reaction (7) as 1 ± 4 kcal. Furthermore, if reasonable assumptions are made about the properties of the methyl and benzyl radicals, the entropy change in the reaction may be calculated and hence the equilibrium between methyl and benzyl radicals and ethylbenzene. On this basis the rate constant of reaction (7) at 182° c has been found to be 10^{12} mole $^{-1}$ c.c. sec. $^{-1}$, E_7 being assumed equal to 0 kcal. This result is probably not very accurate.

It may be supposed that under suitable conditions methyl radicals would combine with atoms, but there is little direct evidence for such reactions. The rate constants will certainly be very dependent upon the total pressure of gas in the system, and it is likely that the "high-pressure" rate will only be approached at several atmospheres, which is not a usual pressure at which to study free radicals. Under the normal conditions of flow pyrolysis, the rates of the reverse reactions, the decompositions of methyl bromide²⁷ and methyl iodide,²⁸ are markedly dependent upon the overall pressure.

The quantitative data on the combination of methyl radicals are summarised in Table 2, where k and A are in mole $^{-1}$ c.c. sec. $^{-1}$. There is very little quantitative information on the rates of combination of other small radicals, though in a fair number of cases the products have been detected. The satisfactory interpretation of a very large amount of information on pyrolysis reactions such as have been described by Szwarc²⁹ has been based

²⁶ *J. Chem. Physics*, 1949, **17**, 431.

²⁷ Schon and Szwarc, *Proc. Roy. Soc.*, 1951, **A**, **209**, 110.

²⁸ Horrex and Lapage, *Discuss. Faraday Soc.*, 1951, **10**, 233.

²⁹ *Chem. Reviews*, 1950, **47**, 75.

upon the supposition that small radicals always combine with zero activation energy. On these grounds, rather than as a result of direct experiments, we must conclude that simple radicals combine with very low activation energies. At the other end of the scale of molecular size it is known¹¹ that growing polymer radicals combine with low activation energies but that the rate constants are usually lower than for small radicals, being of the order of 10^{10} mole⁻¹ c.c. sec.⁻¹.

TABLE 2. *Combination reactions of methyl radicals*

Reaction	<i>k</i> at 182° c	<i>A</i>	<i>E</i> , kcal.
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	4.5×10^{13}	4.5×10^{13}	0 ± 0.7
$\text{CH}_3 + \text{C}_6\text{H}_5\cdot\text{CH}_2 \rightarrow \text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$	(10^{12})	(10^{12})	1 ± 4
$\text{CH}_3 + \text{NO} \rightarrow \text{X}$	2×10^{11} (at 28° c)	2×10^{11} (min.)	4.5 (max.)

Metathetical Reactions of Methyl Radicals.—As yet only the class of metathetical methyl radical reactions represented by the general equation $\text{CH}_3 + \text{RH} \rightarrow \text{CH}_4 + \text{R}$ has been comprehensively studied in a quantitative manner. There are two good reasons for this, the first being that the important products of these reactions from the point of view of a kinetic study, *viz.*, methane and ethane, are fairly easily separated from the rest of the reaction mixture by distillation. Other difficulties apart, an investigation of, for example, the reaction $\text{CH}_3 + \text{C}_5\text{F}_{12} \rightarrow \text{CH}_3\text{F} + \text{C}_5\text{F}_{11}$ would be complicated because CH_3F and C_2H_6 have boiling points which are very close together, so a mass-spectrometer is needed for analysis. The second reason is that our knowledge of the dissociation energies of C-H bonds is more extensive²⁹ than of those between any other two atoms. It has long been thought that there should be a relation between the strength of a bond and the ease with which the atom attached by the bond can be removed by free-radical attack. Much research has been carried out with this possibility in mind.

The first extensive work on reactions of the type mentioned was that of H. S. Taylor with Cunningham³⁰ and with Smith.³¹ They investigated the photolysis of dimethylmercury in the presence of hydrogen, deuterium, ethane, *n*-butane, 2-methylpropane, and neopentane and several unsaturated and aromatic compounds. It has been shown³² that in the majority of cases not very much reliance can be placed upon the quantitative aspects of the work, but the general pattern of the results which they obtained was undoubtedly correct. They found that the activation energy for the reaction of methyl with an alkane containing only primary hydrogen atoms was greater than that for reaction with one containing secondary hydrogen atoms which in turn was greater than that for one containing a tertiary

³⁰ *J. Chem. Physics*, 1938, **6**, 359.

³¹ *Ibid.*, 1939, **7**, 390; 1940, **8**, 543.

³² Steacie, Darwent, and Trost, *Discuss. Faraday Soc.*, 1947, **2**, 79; Trotman-Dickenson and Steacie, *J. Phys. Colloid Chem.*, 1951, **55**, 908.

hydrogen. In addition it was found that the reaction with toluene and propene was rapid, while that with benzene was slow. All these points have been verified by later investigations.

Shortly afterwards, Allen³³ used the photolysis of acetone to investigate the reactions of methyl with propane. The investigation was cursory and the results obtained are not of quantitative significance.

In the last few years a large number of methyl-radical reactions of this type have been investigated, chiefly at the University of Rochester, N.Y., and in the laboratories of the National Research Council of Canada in Ottawa. The results were obtained by the methods outlined above. All of the results which are suitable for tabular presentation are included in Tables 3 and 4. Before considering their significance, we will try to assess their accuracy.

TABLE 3. *Reactions of methyl radicals with hydrogen*

Radical source	Hydrogen isotope	E , kcal.	k (at 182° c) $\times 10^{-4}$	$A \times 10^{-10}$	Ref.
HgMe ₂ . . .	H ₂	9.3 \pm 0.5	14	30	34
Acetone . . .	H ₂	9.2 \pm 0.3	5	15	35
CdMe ₂ . . .	H ₂	13 \pm 2	14	2500	36
Acetone . . .	H ₂	13.2 \pm 0.4	1.5	300	37
Acetaldehyde .	H ₂	15.3 \pm 1.0	25	60,000	37
Acetone . . .	D ₂	11.7 \pm 0.2	1.5	70	35
Acetone . . .	D ₂	14.3 \pm 0.6	0.5	300	37
Acetone- <i>d</i> ₆ . .	H ₂	10.2 \pm 0.2	6	50	35
Acetone- <i>d</i> ₆ . .	D ₂	10.9 \pm 0.3	2	40	35

The most remarkable feature of the figures is the excellence of the agreement obtained by different workers using different sources of methyl radicals and usually different types of radiation when the same substance is photolysed. This gives us great confidence that the results are accurate and that no complications due to "hot" radicals arise. The rate constant k at 182° c is the most directly determinable quantity; this temperature is chosen as being near the middle of the temperature range of most investigations. Different workers usually agree on the magnitude of this rate within a factor of 1.5. In a series of experiments values can usually be reproduced to within $\pm 10\%$. The probable errors in the activation energies are given in the table; these errors are derived solely from the deviations of the points from the Arrhenius relationship; no weight is given to uncertainties in the assumed mechanism. The values for the activation energy are based on $E_2 = 0$ kcal., and the values of A_1 on $A_2 = 4.5 \times 10^{13}$ moles⁻¹ c.c. sec.⁻¹. It should be noted that errors in the differences of

³³ J. Amer. Chem. Soc., 1941, **63**, 708.

³⁴ Phibbs and Darwent, *Trans. Faraday Soc.*, 1949, **45**, 541.

³⁵ Majury and Steacie, *Discuss. Faraday Soc.*, 1953, **14**.

³⁶ Anderson and H. A. Taylor, *J. Phys. Chem.*, 1952, **56**, 498.

³⁷ Davison and Burton, *J. Amer. Chem. Soc.*, 1952, **74**, 2307.

TABLE 4. *Metathetical reactions of methyl radicals**

Reactant	Radical source †	<i>E</i> , kcal.	<i>k</i> × 10 ⁻⁶	<i>A</i> × 10 ⁻¹⁰	Ref.‡
Alkanes					
Methane	Acetone- <i>d</i> ₆	12.8	0.17	(Assumed)	38
Ethane	Acetone- <i>d</i> ₆	10.4 ± 0.4	2.0	19	39
neoPentane	Acetone and acetone- <i>d</i> ₆	10.0 ± 0.3	3.3	20	39
2 : 2 : 3 : 3-Tetramethylbutane	Acetone- <i>d</i> ₆	9.5 ± 0.4	5.2	17	39
<i>n</i> -Butane	Acetone	8.3 ± 0.2	11	11	39
	HgMe ₂	8.2 ± 0.5	22	18	40
	HgMe ₂	9.5 ± 0.5	10	33	40
	HgMe ₂	—	13	—	31
<i>n</i> -Pentane	Acetone	8.1 ± 0.2	14	10	39
<i>n</i> -Hexane	Acetone	8.1 ± 0.2	17	12	39
2-Methylpropane	Acetone	7.6 ± 0.2	22	10	39
	HgMe ₂	7.3 ± 0.3	16	6	41
	Azomethane	6.6 ± 0.3	10	2	42
2 : 3-Dimethylbutane	Acetone	6.9 ± 0.2	35	7	39
	Acetone- <i>d</i> ₆	7.8 ± 0.4	40	21	39
2 : 3 : 4-Trimethylpentane	Acetone- <i>d</i> ₆	7.9 ± 0.4	34	20	39
Alkenes					
Ethene	Acetone- <i>d</i> ₆	10.0 ± 0.4	2.9	17	43
Propene	Acetone- <i>d</i> ₆	7.7 ± 0.4	12	6	43
But-2-ene	Acetone- <i>d</i> ₆	7.7 ± 0.4	30	14	43
2-Methylprop-2-ene	Acetone- <i>d</i> ₆	7.3 ± 0.4	26	8	43
2 : 3-Dimethylbut-2-ene	Acetone- <i>d</i> ₆	7.8 ± 0.4	76	40	43
But-1-ene	Acetone- <i>d</i> ₆	7.6 ± 0.4	34	15	43
Pent-1-ene	Acetone- <i>d</i> ₆	7.6 ± 0.4	35	15	43
3-Methylbut-1-ene	Acetone- <i>d</i> ₆	7.4 ± 0.4	53	18	43
Alkynes					
But-2-yne	Acetone- <i>d</i> ₆	8.6 ± 0.4	33	42	44
But-1-yne	Acetone- <i>d</i> ₆	9.1 ± 0.4	34	76	44
Cyclanes					
<i>cyclo</i> Propane	Acetone- <i>d</i> ₆	10.3 ± 0.4	1.1	9	44
	HgMe ₂	10.2 ± 1.0	1.5	12	45
<i>cyclo</i> Butane	Acetone- <i>d</i> ₆	9.3 ± 0.4	11	28	44
<i>cyclo</i> Pentane	Acetone and acetone- <i>d</i> ₆	8.3 ± 0.2	24	24	44
<i>cyclo</i> Hexane	Acetone	8.3 ± 0.2	22	22	44
Aromatic hydrocarbons					
Benzene	Acetone- <i>d</i> ₆	9.2 ± 0.4	1.0	2.5	44
Toluene	Acetone- <i>d</i> ₆	8.3 ± 0.3	14	14	44
	HgMe ₂	7 ± 2	5	1	31
	DTBP	11 ± 2	—	—	46
Alcohols					
Methanol	Acetone	8.2 ± 0.2	6	4.8	44
	HgMe ₂	8.2 ± 0.5	5	4.4	45
Ethanol	Acetone- <i>d</i> ₆	8.7 ± 0.4	20	29	44
Propan-2-ol	Acetone- <i>d</i> ₆	7.3 ± 0.4	31	10	44

* Values of *k* refer to 182° c, and both *k* and *A* are expressed in terms of moles c.c. sec.⁻¹.

† DTBP = Di-*tert*.-butyl peroxide.

‡ Where this mark is appended to the reference it indicates that the quantities were not calculated in this manner by the original authors.

TABLE 4. *Metathetical reactions of methyl radicals** (continued)

Reactant	Radical source †	E, kcal.	$k \times 10^{-6}$	$A \times 10^{-10}$	Ref. ‡
Amines and imines etc.					
Methylamine	Acetone- d_6	8.4 ± 0.4	19	20	44
Dimethylamine	Acetone- d_6	7.2 ± 0.4	70	19	44
Ethyleneimine	DTBP	4.8 ± 0.3	200	5	47
Trimethylamine	Acetone- d_6	8.8 ± 0.4	44	70	44
Ammonia	Acetone- d_6	10.0 ± 0.4	1.2	7	44
Azomethane	Azomethane	7.6	~ 20	~ 10	42
Ethers and epoxides					
Dimethyl ether	Acetone	9.5 ± 0.2	9	30	44
	HgMe ₂	8.4 ± 1.5	9	10	45
	CH ₂ O·CH ₃	10 ± 2	12	70	7‡
Diisopropyl ether	Acetone- d_6	7.3 ± 0.4	38	12	44
Ethylene oxide	HgMe ₂	9.0 ± 1.0	1.5	3	48
	HgMe ₂	9.6 ± 2	2.8	11	45
Aldehydes					
Acetaldehyde	DTBP	8.0 ± 0.3	220	90	49
Ketones					
Acetone	Acetone	9.7 ± 0.1	10	40	50
	Acetone	9.6 ± 0.4	8	30	51‡
	Acetone	9.5 ± 0.2	11	40	17
	DTBP	9.5 ± 1.0	9	27	52
	Acetone- d_6	10.3 ± 0.2	4	40	50
Acetone- d_6	Acetone- d_6	10.6 ± 0.3	6	70	35
	Acetone- d_6	7.1 ± 0.2	17	5	53
Diacetyl					
Peroxides					
Di-tert.-butyl peroxide . .	DTBP	(15)	2	(3000)	47‡
Metal alkyls					
Dimethylmercury	HgMe ₂	9.0 ± 0.5	10	20	54
	HgMe ₂	11.0	3	40	41
Dimethylcadmium	CdMe ₂	(14)	2	(700)	36
Halogenated methanes					
Methyl fluoride	Acetone	8.7 ± 0.3	25	40	55
Methylene fluoride	Acetone	6.2 ± 0.3	30	3	55
Methyl chloride	Acetone	9.4 ± 0.3	25	70	55
Methylene chloride	Acetone	7.2 ± 0.3	60	20	55
Chloroform	Acetone	5.8 ± 0.3	100	6	55
	Acetone	6.8			56
Methyl bromide	Acetone	10.1 ± 0.3	40	300	55
Methylene bromide	Acetone	8.7 ± 0.3	100	150	55
Hydrogen halide					
Hydrogen chloride	Acetone	2.1	2×10^5	200	56

* Values of k refer to 182° c, and both k and A are expressed in terms of moles⁻¹ c.c. sec.⁻¹.

† DTBP = Di-tert.-butyl peroxide.

‡ Where this mark is appended to the reference it indicates that the quantities were not calculated in this manner by the original authors.

activation energies derived from a series of experiments on different compounds may often be much less than the errors in the *absolute* values. When this consideration is of importance for the interpretation of the experimental data attention will be drawn to the matter.

The results given in Table 3 for the reaction of methyl with hydrogen are taken straight from the original papers and show the confused state of the literature.^{*} The random experimental errors are quite likely to be on the low side but the discrepancies are too large to be assigned to this cause alone. Wijnen and Steacie⁵⁷ have shown that if, of those runs done by Davison and Burton,³⁷ one takes notice only of those in which the percentage conversion of the reactants was low and the photolysis was not likely to be complicated by side reactions, then the work gives a value of 10.5 ± 1 kcal./mole for the activation energy of the reaction. In their opinion all the most reliable published work leads to a value of 10.0 ± 0.5 kcal./mole for the activation energy. Unfortunately, this solution does not resolve all the difficulties, for the activation energy of the reaction



appears to be at least 12 kcal./mole, and therefore the back reaction must have an activation energy of at least 13 kcal./mole. No satisfactory explanation of this discrepancy has yet been given.

Several series of compounds have been studied sufficiently fully for it to be possible to draw certain conclusions about the trends in reactivity within the groups. The best investigated of all these series is that of the alkanes. Here it is apparent that the compounds fall into three groups of activation energies for the reaction with methyl of (i) about 10; (ii) about

³⁸ Trotman-Dickenson and Steacie, *J. Phys. Colloid Chem.*, 1951, **55**, 908.

³⁹ Trotman-Dickenson, Birchard, and Steacie, *J. Chem. Physics*, 1951, **19**, 163.

⁴⁰ Gomer, *J. Amer. Chem. Soc.*, 1950, **72**, 201.

⁴¹ Rebbert and Steacie, personal communication.

⁴² Jones and Steacie, personal communication.

⁴³ Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1951, **19**, 169.

⁴⁴ *Idem*, *ibid.*, p. 329.

⁴⁵ Phibbs and Darwent, *Canadian J. Res.*, 1950, **B**, **28**, 395.

⁴⁶ Roberts and Szwarc, *Trans. Faraday Soc.*, 1950, **46**, 625.

⁴⁷ Brinton and Volman, *J. Chem. Physics*, 1952, **20**, 25.

⁴⁸ Gomer and W. A. Noyes, jun., *J. Amer. Chem. Soc.*, 1949, **71**, 3390.

⁴⁹ Brinton and Volman, *J. Chem. Physics*, 1952, **20**, 1053; there is strong evidence that this is the most reliable value, but for a different view see Dodd, *Trans. Faraday Soc.*, 1951, **47**, 56.

⁵⁰ Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1950, **18**, 1097.

⁵¹ Saunders and H. A. Taylor, *ibid.*, 1941, **9**, 616.

⁵² Jacquiss, Roberts, and Szwarc, *J. Amer. Chem. Soc.*, 1952, **74**, 6005.

⁵³ Blacet and Bell, *Discuss. Faraday Soc.*, 1953, **14**.

⁵⁴ Gomer and W. A. Noyes, jun., *J. Amer. Chem. Soc.*, 1949, **71**, 3390.

⁵⁵ Raal and Steacie, *J. Chem. Physics*, 1952, **20**, 578. The error in these results is in some cases probably greater than is indicated because complicating side reactions may have occurred.

⁵⁶ Cvetanović and Steacie, *Canad. J. Chem.*, 1953, **31**, 158.

⁵⁷ *Discuss. Faraday Soc.*, 1953, **14**.

8.2, and (iii) less than 8 kcal./mole, and that these contain, respectively, (i) only primary, (ii) primary and secondary, (iii) primary and tertiary hydrogen atoms. Furthermore, since the A factors do not vary widely, this trend in activation energies is reflected by the trend in the rate constants. Now 2 : 2 : 3 : 3-tetramethylbutane contains three times as many primary hydrogen atoms as ethane, and 2 : 2-dimethylpropane twice as many. Since the three compounds all react with methyl with nearly the same activation energy, the hydrogen atoms in these compounds may be considered equivalent. Similarly, 2 : 3 : 4-trimethylpentane has three reactive tertiary hydrogen atoms, while 2 : 3-dimethylbutane has two and 2-methylpropane has one. We can by inspection decide how many "active" hydrogen atoms there are in an alkane and, after making a very small correction for the presence of less active types of hydrogen atoms in the compound, find by division the reaction rate characteristic of the "active" hydrogen atom. Thus for n -butane there are four "active" hydrogen atoms and six less active primary atoms. By consideration of the results obtained with compounds containing only primary hydrogen atoms, it can be found that the rate constant characteristic of a primary hydrogen atom at 182° c is *ca.* 3×10^6 mole⁻¹ c.c. sec.⁻¹. Hence for n -butane the rate constant characteristic of a secondary hydrogen atom is $\frac{1}{4}[11 - (6 \times 0.3)] = 2.3 \times 10^6$ mole⁻¹ c.c. sec.⁻¹. In this manner Table 5 has been obtained.

TABLE 5. *Rate constants characteristic of various types of hydrogen atoms in alkanes*

Type of hydrogen atom	$10^{-6}k$, characteristic, at 182° c (mole ⁻¹ c.c. sec. ⁻¹ /atom)
Primary	0.3, 0.2, 0.3
Secondary	2.3, 2.0, 2.0
Tertiary	18, 17, 10

This procedure is justified solely by the interesting nature of the results, which show that it is reasonable to regard the different types of hydrogen atom in a molecule as if they were present in separate molecules in a multi-component mixture.

In two recent reviews⁵⁸ reference has been made to a relation suggested by Polanyi between the heat of one reaction in a series and its energy of activation. Polanyi stated that, where there is no resonance stabilisation in the transition complex or a constant amount of stabilisation throughout a series, then for reactions of the type $X + YZ \rightarrow XY + Z$ it may be expected that $E = \alpha H + \text{const.}$, where E is the activation energy and H the heat of the reaction, and α has a value between 0 and 1. The results quoted above indicate that all primary C-H bonds and all secondary C-H bonds are very similar; if this uniformity is accepted, where the evidence is less

⁵⁸ Warhurst, *Quart. Reviews*, 1951, **5**, 44; Bolland, *ibid.*, 1950, **4**, 292.

good, for all tertiary C-H bonds we may generalise Stevenson's electron impact data⁵⁹ as follows:

D(CH ₃ -H)	102 kcal.	D(C-H), secondary	94 kcal
D(C-H), primary	97 kcal.	D(C-H), tertiary	90 kcal

From these figures, heats of reaction can be obtained for the reaction of methyl with each type of hydrogen atom; these values for the heats are plotted against the activation energies in Fig. 1. The value of E for $\text{CH}_3 + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_3$ was not determined directly, as the rate has effectively only been measured at one temperature. The straight line drawn in Fig. 1 is for $\alpha = 0.5$, which would be expected from consideration of symmetry based upon the similarity of the bonds broken and formed

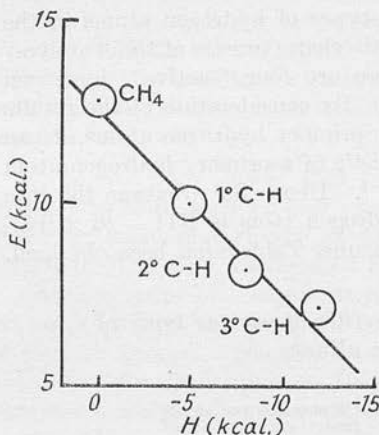


FIG. 1

The relation between activation energy and heat of reaction for the reactions of methyl radicals with alkanes:

$$E = 12.5 + 0.5H.$$

the positive deviation of the value of E for the tertiary hydrogen atom from the line might also be expected. This is the only case in which Polanyi relation has been subjected to direct experimental test.

The striking fact about the results obtained from the study of the reactions of methyl radicals with alkenes is that, apart from ethene, they all react with methyl with the same activation energy within the rather small limits of experimental error (the relative values of the activation energies are here good to 0.2 kcal./mole). It may be seen that, where possible, it is always the α -methylenic hydrogen atom which reacts. Thus there are three "active" hydrogen atoms in propene, twelve in 2:3-dimethylbut-2-ene, two in but-1-ene and one in 3-methylbut-1-ene. In Table 6 are given the rate constants per active hydrogen atom for primary, secondary, and tertiary α -methylenic hydrogen atoms and, assuming a constant value of E of 7.6 kcal., the values are divided by the number of active hydrogen atoms. This table shows, first, that each type of hydrogen atom has a particular rate constant for reaction with methyl in the alkene as well as in the alkane series. Secondly, the changes in reactivity are due to changes in the A factor and not

⁵⁹ *Discuss. Faraday Soc.*, 1951, **10**, 35; for a different view cf. Leigh and Szwarc, *J. Chem. Physics*, 1952, **20**, 407.

activation energy, as was the case with the alkanes. No explanation for this most interesting fact has yet been advanced.

No other series of compounds has been investigated thoroughly apart from the cyclanes, where the variations are of a different kind from those previously considered. It is noteworthy that the variations in rate found among the cyclanes had been previously predicted by Brown⁶⁰ by consideration of the strains involved in the molecule and in the transition state. It is possible, however, that other attractive explanations could be found.

TABLE 6. *Rate constants at 182° C and frequency factors per hydrogen atom characteristic of different types of hydrogen atoms in alkenes (both in mole⁻¹ c.c. sec.⁻¹)*

Type of hydrogen atom	10 ⁻⁴ k/H	10 ⁻¹⁰ A/H
Primary . . .	4, 5, 4, 6	2
Secondary . . .	17, 18	7
Tertiary . . .	53	23

From the results in Table 4 as a whole, three facts stand out. First, that the spread of activation energies is small, only 8 kcal./mole, whereas the spread of C-H bond strengths is between the weakest bond in toluene and that in methane. Secondly, the general rule that primary hydrogen atoms react less readily than secondary, and these in turn less readily than tertiary, holds throughout, as shown by the values of the rate constant/number of "active" hydrogen atoms for each class of compound in Table 7.

TABLE 7. *Rate constants characteristic of various types of hydrogen atom in different classes of compound*

Class of compound :	Alkane	Alkene	Alkyne	Ether	Alcohol
Type of hydrogen atom	10 ⁻⁴ k/H at 182° C (mole ⁻¹ c.c. sec. ⁻¹ /atom)				
Primary	0.3	5	7	1.5	2
Secondary	2.1	17	38	—	10
Tertiary	15	53	—	19	31

Thirdly, although there is a considerable variation in the *A* factors, yet they all, except for two doubtful cases, lie in the range 10^{10.4} — 10^{12.5} as is shown by Fig. 2. This means that the steric factors lie between 10⁻² and 10⁻⁴. The figures show that the concept of reactivity as applied to free-radical reactions is very vague when studies have only been made at one temperature. Whenever possible, activation energies and *A* factors should be determined, and if this cannot be accomplished, great caution should be exercised in interpreting the results.

The rates of three reactions of methyl radicals relative to the rate of

⁶⁰ *J. Amer. Chem. Soc.*, 1951, **73**, 212.

reaction (4) (p. 204) have been studied. The method (described in the section on methods) was first used by Anderson and Kistiakowsky⁶¹ and later by Williams and Ogg.⁶² The later work was considerably more



extensive and involved the determination of the relative rates of reactions

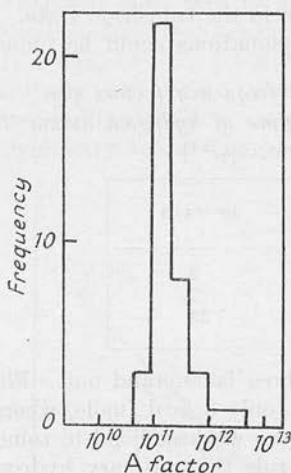


FIG. 2

The frequency of occurrence of A factors for methyl-radical reactions.

(4) and (8), where X is Cl, Br or I, over a range of temperatures. Thus $E_8 - E_4$ and A_8/A_4 were found; the values are given below:

Reaction	$E_8 - E_4$, kcal./mole	A_8/A_4
$\text{CH}_3 + \text{HI}$	0.75	0.23
$\text{CH}_3 + \text{HBr}$	0.95	0.13
$\text{CH}_3 + \text{HCl}$	2.4	0.04

Williams and Ogg considered that "hot" methyl radicals were involved in the reaction with hydrogen chloride, so the meaning of the figures is doubtful. For this reason the results cannot be directly compared with those obtained from the photolysis of acetone in the presence of hydrogen chloride.⁵⁶ The experiments are very difficult to conduct and to interpret so little reliance should be placed upon the precise numerical values obtained. The supposition that reaction (4) takes place on every collision is reasonable but not proven.

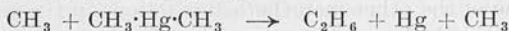
Large numbers of other gas-phase reactions of methyl radicals involving hydrogen abstraction have been postulated but not quantitatively investigated. Steacie¹ lists many of these.

No metathetical reactions of methyl in the gas phase have been quantitatively investigated in which atoms other than hydrogen are abstracted though these certainly occur. Of particular importance are the reactions with the halogens which occur so rapidly that they cannot be studied by present techniques.

⁶¹ *J. Chem. Physics*, 1943, 11, 6.

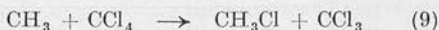
⁶² *Ibid.*, 1947, 15, 696.

Two reactions have been found in which a methyl radical extracts a radical from a molecule. They are



The rate constant of the first is approximately represented by the equation $k = 10^7 e^{-1000/RT}$ and of the second by $k = 4.8 \times 10^{10} e^{-5600/RT}$ mole⁻¹ c.c. sec.⁻¹. Reactions of this type seem to be very rare and until more are found it is not possible to state with what sort of molecules they are likely to occur.

No methyl-radical reactions have been investigated in solution sufficiently fully to determine rate constants. Indeed, apart from the greater analytical difficulties, it is to be expected that in many cases complications may be caused by the fact that two methyl radicals released as a pair from a molecule by photolysis (as in the case of acetone and dimethylmercury) may be caged in and have a greater probability of combining than would be expected from the overall concentration of methyls and the rate constants in the gas phase, so that the rate of formation of ethane is not a reliable guide to radical concentration. Edwards and Mayo¹³ have investigated the rates



of a number of reactions of type (1) relative to the rate of reaction (9) at 100° c. The radicals were produced by pyrolysis of acetyl peroxide, and the reactions were followed by the relative rates of production of methane and methyl chloride. The rate constants k_1/k_9 in solution are compared in Table 8 with the rate constants, k_1 , determined by Trotman-Dickenson and Steacie⁴⁴ for the five compounds common to the two investigations (the k_1 value for oct-1-ene was assumed equal to $k_{\text{pent-1-ene}} + k_{n\text{-pentane}} - k_{\text{ethane}}$). The table shows a remarkable parallelism between the two sets of data: *cyclohexane* apart, the constancy of the last column is much

TABLE 8. *Relative rate constants for the reactions of methyl radicals in the gas phase and in solution*

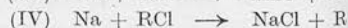
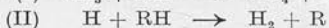
Compound	k_1/k_9 (solution) at 100° c	$10^{-4}k_1$ (gas) at 100° c, mole ⁻¹ c.c. sec. ⁻¹	$10^{-4}k_1$ (gas) k_1/k_9 (solution)
Benzene	0.04	0.091	2.3
Acetone	0.40	1.0	2.5
Toluene	0.75	1.9	2.5
Oct-1-ene	3.2	7.7	2.4
<i>cycloHexane</i> . . .	4.5	3.4	0.8

better than the reliability of the figures would lead one to expect. The result is of importance because it is the first case in which a free-radical reaction has been accurately studied in the gas phase and in solution. However, there is some evidence that the reacting species in Mayo's work is not a methyl radical at all but the $\text{CH}_3\cdot\text{CO}\cdot\text{O}$ radical. This difficulty is characteristic of reactions in solution.

The metathetical reactions of other radicals or atoms have been very little investigated in the gas phase or in solution. In Table 9 are collected the data on some of the other metathetical reactions in the gas phase which may be compared with the methyl reactions. The information is fragmentary, but as far as it goes it leads us to suppose that the gradations in the reactivity of methyl radicals with various compounds will be reflected in the reactivity of other radicals with the compounds. On the other hand there are some notable exceptions to this rule, and even for the reactions presented in the table there exist data which conflict with this conclusion. In solution the transfer-reaction velocity constants which have been measured for the thermal polymerisation of styrene in various solvents⁶⁸ correspond to metathetical reactions of the polystyrene radicals. In this case, where an extreme difference in molecular size is involved, there appears to be little correlation with the methyl reactions.

TABLE 9. *Activation energies (in kcal./mole) of various metathetical reactions*

R	Reaction							
	I	Ref.	II	Ref.	III	Ref.	IV	Ref.
H	10	64	5	65	17.6	67	6.1	70
CH ₃	12.8	64	13	66	18.3	68	10.0	70
C ₂ H ₅	10.4	64	9	66	13.6	69	9.4	70
Bu ^s	8.3	64	7.2	66	—	—	8.6	70
Bu ^t	7.6	64	6.3	66	—	—	7.8	70
CH ₂ :CH·CH ₂	7.7	64	5.0	66	—	—	5.3	70
CH ₃ :CH:CH·CH ₂	7.7	64	5.0	66	—	—	—	—



Addition Reactions of Methyl Radicals.—Large numbers of addition reactions of methyl radicals of the type $\text{CH}_3 + \text{X}=\text{Y} \rightarrow \text{CH}_3\text{-X-Y}$ have been identified, with a wide variation of the groups X and Y. A list of these types is given below. For only one addition reaction, however,

Type of multiple bond	Example	Type of multiple bond	Example
C=C	Many alkenes	C=O	Carbon monoxide
C≡C	Ethyne	N=N	Azomethane
C=C-C=C	Butadiene	O=O	Oxygen

has the velocity constant been determined, *viz.*, for $\text{CH}_3 + \text{O}_2 \rightarrow \text{product}$ Marcotte and Noyes⁷¹ found the rate constant for this reaction by com-

⁶³ Burnett, *Quart. Reviews*, 1950, **4**, 292.

⁶⁴ See Tables 3 and 4.

⁶⁵ Farkas and Farkas, *Proc. Roy. Soc.*, 1935, **A**, **152**, 124.

⁶⁶ Darwent and Roberts, *Discuss. Faraday Soc.*, 1953, **14**.

⁶⁷ Bodenstein and Lütke Meyer, *Z. physikal. Chem.*, 1935, **114**, 208.

⁶⁸ Kistiakowsky and Van Artsdalen, *J. Chem. Physics*, 1944, **12**, 469.

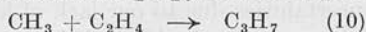
⁶⁹ Anderson and Van Artsdalen, *ibid.*, p. 479.

⁷⁰ Warhurst, *Quart. Reviews*, 1951, **5**, 44.

⁷¹ *J. Amer. Chem. Soc.* 1952, **74**, 783.

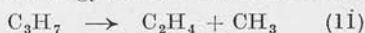
paring the rate of disappearance of oxygen from an illuminated acetone-oxygen mixture with the rate of production of methane. They found the activation energy of the reaction to be 0 ± 0.5 kcal./mole and that $A = 8 \times 10^{10}$ mole⁻¹ c.c. sec.⁻¹.

The reason why it has been impossible to determine the velocity constant of reaction (10) is that the propyl radical rapidly reacts with another



ethene molecule, combines or disproportionates with a methyl, propyl, or higher radical, or, at temperatures above 520° K, decomposes at an appreciable rate. The situation is thus extremely complicated and cannot be sorted out by our present techniques. An attempt has been made⁷² to give a general kinetic treatment of the reactions which occur when acetaldehyde is photolysed in the presence of a number of different alkenes. No reliable rate constants for the individual steps have been derived by this method, and the study illustrates clearly the great difficulties which have to be overcome before quantitative results can be obtained by this straightforward approach.

Some information about the addition of methyl radicals to alkenes may be obtained indirectly by studying the kinetics of the reverse reaction. Thus although it has not been possible to determine the activation energy of (10), yet the activation energy of the reverse reaction (11) can be measured.



This has been done by Bywater and Steacie,^{3, 4, 5} who produced the propyl radicals by mercury photosensitisation. They found $E = 20$ kcal./mole. If the $\text{C}_3\text{H}_7\text{-H}$ and $\text{CH}_3\text{-H}$ bond strengths are known, it is possible to calculate ΔH for reaction (11) from well-established thermochemical data. The data due to Stevenson⁴⁵ on the $\text{CH}_3\text{-H}$ and primary, secondary, and tertiary C-H bonds, which have been referred to above, can be used for this purpose. Hence $\Delta H = 23$ kcal.

Now $\Delta H = E_{11} - E_{10}$, therefore $E_{10} = -3$ kcal. In Table 10 all the information is set out which can be calculated in this way from the published data for the addition of hydrogen atoms or methyl or ethyl radicals to alkenes. All the data on the decomposition of the

TABLE 10. *Activation energies (kcal./mole) for the addition of radicals to alkenes*

Alkene radical	Hydrogen-atom	Methyl radical	Ethyl radical
Ethene	+ 2	- 3	+ 2
Propene	+ 1, (+ 4)	- 1, (+ 2), - 3	—
2-Methylpropene	- 1, (- 8)	—	—

radicals come from the papers by Bywater and Steacie; Stevenson's bond strengths⁵⁹ have been used. When the decomposition mechanism assumed

⁷² Raal, Danby, and Hinshelwood, *J.*, 1949, 2225.

involves the internal rearrangement of one of the fragments, the result is placed in parentheses as being of doubtful value. The results in the table are uncertain to about ± 4 kcal., so the only conclusion which can be drawn is that these addition reactions have very small activation energies.

The entropy change in the equilibrium formed by reactions (10) and (11) for example, can be calculated with a reasonable degree of confidence because most of the uncertainties due to our lack of knowledge of the properties of the radicals occur on both sides of the equilibrium. So if A_7 and E_{11} are known we can calculate A_{10} and E_{10} from bond-strength and thermodynamic data. Thus we find⁷³ that the additions of methyl radicals to ethylene and propene have frequency factors of the order of 10^6 mole⁻¹ c.c. sec.⁻¹. This remarkable conclusion is supported by the fact that similar calculations for the reactions of hydrogen atoms give results which are in good agreement with the measured rates.

⁷³ Trotman-Dickenson, *Discuss. Faraday Soc.*, 1953, 14.

Entropy Changes in Free Radical Reactions

A. F. TROTMAN-DICKENSON

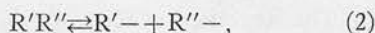
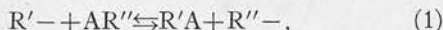
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(Received August 28, 1952)

The entropies of alkyl and other simple free radicals may be estimated with sufficient accuracy to make informative calculations about the equilibria involved in the reactions of these radicals. Such calculations have been made for metathetical reactions, the decomposition of saturated molecules, and the decomposition of free radicals. The method provides a means of obtaining knowledge about reactions which are not readily susceptible to direct experimental investigation. The deviations of the frequency factors of some unimolecular decompositions from a value of $10^{13\pm1}$ are discussed.

ONE of the principal reasons for studying free radical reactions is that they are, because of their formal simplicity, very suitable for testing theories of chemical kinetics.

Free radical reactions may be divided into three classes represented by the equilibria (1), (2), and (3)



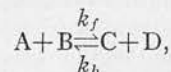
Type (1) represents a metathetical reaction, type (2) represents the decomposition of a saturated molecule and the combination of two radicals, and type (3) represents the addition of a radical to a double bond and the decomposition of a radical into a smaller radical and an unsaturated molecule. At the present time examples of all these types of free radical reaction are known; in some cases it has been possible to measure their rate constants and even to obtain their frequency factors and activation energies, but in very few cases have the forward and reverse processes for the same reaction been quantitatively studied. This discussion will be confined to a consideration of the "temperature independent" factors of reactions of the types (1), (2), and (3).

It has been found that the Arrhenius equation

$$k = A \exp(-E/RT)$$

adequately describes the variation of the velocity constant of a gas reaction with temperature (the symbols

have their usual meaning). Hence for the reaction



$$-RT \ln k_f/k_b = (E_f - E_b) - RT \ln A_f/A_b = \Delta H - T\Delta S$$

$$R \ln A_f/A_b = \Delta S.$$

This relation is strictly true if the activation energy is defined by

$$RT^2(d \ln k/dT) = E,$$

and the temperature independent factor is defined by

$$RT \ln A = \partial(RT^2 \ln k)/\partial T.$$

These definitions relate to a particular temperature, whereas experimentally A and E are derived from the integrated form of the Arrhenius equation. However, it has been found that for gas phase reactions, these two derivations give the same values for A and E within the limits of experimental error. In addition the most popular theories indicate that for bimolecular and unimolecular reactions, the form of the temperature dependence of the A factors should be the same and hence the ratio A_f/A_b will be temperature independent. This type of treatment results from the work of Van t'Hoff and has been recently used by Dainton and Ivin¹ when discussing polymerization reactions, though they arrive at the same expression by consideration of

¹ F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.* **46**, 331 (1950).

the theory of absolute reaction rates, which is unnecessary.

Here we will calculate values of ΔS and hence of A_f/A_b for a number of reactions for which either A_f or A_b are known. The entropies of the radicals are often not known accurately, but because of the symmetry of many of the reactions, many of the errors which may occur resulting from arbitrary assumptions about the character of the radicals balance out and fairly definite conclusions may be drawn. Unless it is specifically stated to the contrary, the calculations have been carried out using entropies at 298°K; where it is convenient the calculations have been repeated for temperatures closer to those at which the reactions were studied experimentally. It can be seen that this does not alter the character of the results. The evaluation of entropy changes involves a knowledge of three species (a) of ordinary saturated molecules, (b) of atoms, and (c) of free radicals.

(a) The entropies of ordinary saturated molecules are taken from the tables published by the National Bureau of Standards.²

(b) The entropies of atoms may be calculated to the desired accuracy by the use of standard methods.

(c) The entropies of the large free radicals R, that is, other than ethyl and methyl, are taken as being the same as those of the compounds RH with an allowance made of the electron degeneracy of the radical owing to the presence of an unpaired electron. In most cases this is probably a very good approximation, for the translational entropy because of the very small differences in mass; for the rotational entropy because of the small change in the moments of inertia and because the symmetry number is unlikely to vary by more than a factor of two; and for the vibrational entropy because although an inversion vibration analogous to that in ammonia may make a considerable contribution to the vibrational entropy of an alkyl radical, this entropy is only a small fraction of the total. As an illustration of this point let us consider the entropy of a methyl radical (neglecting for the moment the contribution of the electron degeneracy). We have the following figures, at 298°K.

$$S^0(\text{methane}) = 44.5 \text{ eu}, \quad S^0(\text{ammonia}) = 45.9 \text{ eu},$$

for a planar methyl radical (symmetry number 6)

$$S^0_{\text{trans}}(\text{methyl}) = 34.1 \text{ eu}, \quad S^0_{\text{rot}}(\text{methyl}) = 9.9 \text{ eu},$$

for a methyl radical with a very high inversion frequency

$$S^0_{\text{trans}} + S^0_{\text{rot}} + S^0_{\text{vib}}(\text{methyl}) = 44.1 \text{ eu},$$

for a methyl radical with very low inversion frequency

$$S^0_{\text{trans}} + S^0_{\text{rot}} + S^0_{\text{vib}}(\text{methyl}) = 45.5 \text{ eu}.$$

From these figures it can be seen that the value of 45.5 eu which has been adopted here for the total

² Natl. Bur. Standards (U. S.), Circ. C. 461, 1947, Washington D. C.

entropy of the methyl radical, may be too low but can hardly be too high.

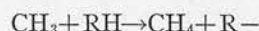
Similarly the value adopted for the ethyl radical of 56.3 eu may be seen to be about as small a value as could reasonably be selected when compared with $S^0\text{C}_2\text{H}_6 = 54.9 \text{ eu}$, $S^0\text{C}_2\text{H}_4 = 52.5 \text{ eu}$, and $S^0\text{CH}_3\text{NH}_2 = 57.7 \text{ eu}$.

We can now use these values to derive the A factors of reactions which are not in general experimentally accessible. It will be seen that in some cases there is an experimental value which agrees satisfactorily with that calculated.

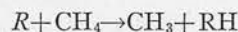
1. METATHETICAL REACTIONS

(a) The Reactions of Methyl Radicals with Alkanes

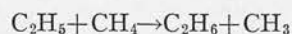
A large number of reactions of the type



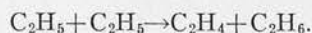
have been studied³ and it has been found⁴ that the A factors are of the order of 10^{11} (all velocity constants are given in g mole, cc and sec). Since the entropy change in these reactions is almost zero, reactions of the type



will also have A factors of the order of 10^{11} . Hence the A factor for the reaction

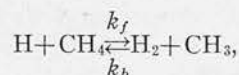


may be expected to be of the order of 10^{11} . It is therefore very surprising that Ivin and Steacie⁵ find that $A = 10^{13.3}$ for the very similar reaction



(b) The Reactions of Hydrogen Atoms with Alkanes

In these reactions the entropy change is not zero because of the large difference between the entropies of the hydrogen atom and the hydrogen molecule. Rather exact calculations may be made for the equilibrium



because of the simplicity of the species. We find that $A_f \geq 10A_b$ in good agreement with the latest experimental data which indicates that A_f is between 10 and 100 times as great as A_b .⁶ It has often been assumed when the results of hydrogen atom reactions studied by the Wood-Bonhoeffer method are considered

³ A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.* **19**, 329 (1951).

⁴ R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.* **19**, 85 (1951).

⁵ K. J. Ivin and E. W. R. Steacie, *Proc. Roy. Soc. (London)* **A208**, 25 (1951).

⁶ E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1947); T. G. Majury and E. W. R. Steacie, *J. Chem. Phys.* **20**, 197 (1952).

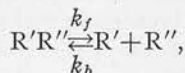
that reactions of the type



have frequency factors of the order of 10^{13} . If that assumption is correct the frequency factors of the back reactions for alkyl radicals should be 10^{12} , since $A_b/A_f \approx 1/10$.

2. UNIMOLECULAR DECOMPOSITIONS

Szwarc and his collaborators have recently measured the rates of a large number of reactions of the type



and in some cases have been able to measure the frequency factors of the reactions. When this has been impossible very fruitful interpretations of the data have been obtained by assuming that A_f is constant for a series of similar reactions in which R' is unchanged. We will consider two series, the alkyl benzenes and the bromomethanes.

(a) The Alkyl Benzenes

In treating the alkyl benzenes it has been assumed that the entropy of the benzyl radical is the same as that of toluene, however, this doubtful assumption does not affect conclusions about variations among members of the series. The results are given in Table I. The variation of $A_b(\text{calc})$ in this table is not in agreement with the general belief that the association of more complex radicals will involve a lower A factor. To obtain a value of A_b of 10^9 would mean that A_f would be 3×10^{12} , this value of A_f combined with the experimental value for k_f leads to an activation energy consistent with an equality of strengths for the C_2H_5-H and $n-C_3H_7-H$ bonds, which is a more reasonable result than that of $D(C_3H_7-H) - D(C_2H_5-H) = 4$ kcal given by Szwarc and Leigh (see Table I, references c and d).

(b) The Bromomethanes

Similar calculations for the decompositions of the series of bromomethanes⁷ have been made on the assumption that $S_{RH} = S_R$. A_f has been taken as 10^{13} , there being good experimental evidence that this value is correct for CH_3Br and CCl_3Br . The results in the table are probably reliable and form a series which conforms with the general idea that the association of more complex radicals involves lower A factors:

Reaction	A
$CH_3 + Br$	4×10^{11}
$CH_2Br + Br$	1×10^{11}
$CHBr_2 + Br$	3×10^{10}
$CBr_3 + Br$	7×10^9

TABLE I. A factors for the decomposition of alkyl benzenes.

Substance	$A_f(\text{expt})$	A_f/A_b at 298°K	A_f/A_b at 1000°K	$A_b(\text{calc})$ 1000°K
Toluene	10^{13} ^a	40	240	4×10^{10}
Ethyl benzene	10^{13} ^b	1000	2900	3×10^9
<i>n</i> -Propyl benzene	3×10^{12} ^c	2500	2300	1×10^9
<i>n</i> -Butyl benzene	3×10^{14} ^d	3000	3000	1×10^{11}

^a M. Szwarc, J. Chem. Phys. 16, 128 (1948).

^b M. Szwarc, J. Chem. Phys. 17, 431 (1949).

^c C. H. Leigh and M. Szwarc, J. Chem. Phys. 20, 403 (1952).

^d C. H. Leigh and M. Szwarc, J. Chem. Phys. 20, 407 (1952).

(c) The Combination of Alkyl Radicals

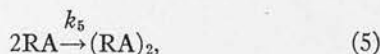
Only two rate constants and A factors have been determined for the combination of radicals in the gas phase. They relate to the combination of methyl and the combination of ethyl radicals. From these results the *minimum* values of the A factors for the symmetrical decomposition of ethane and *n*-butane may be calculated with certainty and are given in the table.

	A	This work	Original authors
Decomposition of ethane		1×10^{17}	2×10^{15}
Decomposition of butane		1.5×10^{17}	6×10^{15}

The values given by the original authors are rather low because Ivin and Steacie⁵ seem to have chosen an impossibly low value for the entropy of the ethyl radical, and Gomer and Kistiakowsky⁴ used the equilibrium constant calculated by Glasstone, Laidler, and Eyring,⁸ who made no allowance for the electron degeneracy of the free radicals and so obtained an answer which is probably too small.

3. THE DECOMPOSITION OF FREE RADICALS

Bywater and Steacie⁹ have studied the decomposition of the free radicals produced by the mercury photo-sensitization of ethane, propane, and 2-methyl propane and determined the activation energies of the decompositions on the assumption that the dimerization of the free radicals requires no activation energy. In each of these cases it is possible to estimate from the experimental data the number of alkyl radicals decomposing and the number dimerizing, the error being of the order of 20–30 percent. If these two quantities are known, then it is possible¹⁰ to calculate the relative values of the rate constant k_{4f} and k_5 for the reactions (4) and (5) by using the



⁸ Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 263.

⁹ S. Bywater and E. W. R. Steacie, J. Chem. Phys. 19, 172, 319, 326 (1951).

¹⁰ A. F. Trotman-Dickenson, J. Chem. Phys. 19, 261 (1951).

⁷ M. Szwarc and A. H. Schon, Proc. Roy. Soc. (London) A209, 110 (1951).

formula $dR/dt/d(RA)_2/dt = k_{4f}/k_5^{\frac{1}{2}}$. Since the activation energy of reaction (4f) is known a maximum value of A_{4f} may be obtained by supposing reaction (5) to take place on every collision. The annexed table given the values found for A_{4f} .

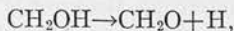
Reaction	A_f	A_b	
$C_2H_5 \rightarrow C_2H_4 + H$	2×10^{14}	2×10^{13}	(6)
$C_3H_7 \rightarrow C_2H_4 + CH_3$	3×10^9	6×10^6	(7)
$C_4H_9 \rightarrow C_3H_6 + CH_3$	1×10^9	1×10^5	(8)

By the methods outlined above the entropy changes in these reactions may be found, and hence A_{4b} calculated; the values found are given in the table. Full experimental data to check these calculations are not yet available, but two pieces of work provide some comparison.

Melville and Robb¹¹ have found that the collision yield for the reaction of hydrogen with ethylene at room temperature is 10^{-3} , this would agree with the above results if the activation energy for the reaction is 3 kcal. From Bywater and Steacie's activation energy for the decomposition, and Stevenson's¹² bond strengths the activation energy for the addition may be calculated as 2 kcal.

Trotman-Dickenson and Steacie¹³ found that at 180°C the addition of a methyl radical to ethylene took place at the same speed to within a factor of two or three as the abstraction of a hydrogen atom. The rate constant for the abstraction reaction is 3×10^6 g mole⁻¹ cc sec⁻¹. Our slight knowledge of bond strengths and activation energies for the decomposition of radicals indicates that reaction (7_b) will have very small or zero activation energy. If the reaction requires zero activation energy then $A_{7b} = 3 \times 10^6$ in remarkable agreement with the value calculated above.

The frequency factors for the decomposition of the propyl and butyl radicals differ markedly from the value of 10^{13} which has been regarded as a norm. Two other cases of such low frequency factors in similar reactions are known, as has been pointed out by Trotman-Dickenson¹⁰; they are the decomposition of the radicals of dimethyl ether and of methyl alcohol,



where the maximum possible values for the A factors

¹¹ H. W. Melville and J. C. Robb, Proc. Roy. Soc. (London) A202, 181 (1950).

¹² D. P. Stevenson, Disc. Faraday Soc. 10, 35 (1951).

¹³ A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys. 19, 169 (1951).

were found to be 1.5×10^{10} and 1.7×10^{10} , respectively. In all of these cases the errors are probably quite large and amount to about one power of ten. Consequently although the fact that the frequencies factors are very low is well established, little reliance can be placed on the exact numerical values.

The decomposition of ethane and butane discussed above are examples of the opposite phenomenon for they have very high frequency factors. The experimental data seem very reliable and a minimum value for the frequency factor has been deliberately calculated. A further somewhat similar example of a high frequency factor has recently been confirmed by Carrington and Davidson,¹⁴ who find that the reaction



has a frequency factor of about 10^{16} if the reverse reaction has no energy of activation.

These two classes of deviation of the A factor of a reaction from the accepted value of $10^{13 \pm 1}$ raise considerable problems. It may be that special explanations apply to these cases, for example, the decompositions of radicals in which one fragment has to rearrange to form an unsaturated compound are slightly reminiscent of the cases of *cis-trans* isomerism in which low frequency factors were found. Harman and Eyring¹⁵ suggested that this effect might be the cause of the A factors which are found for the propagation reactions in polymerizations, those reactions are the reverse of the decompositions. However, Baxendale and Evans¹⁶ have shown that in this case the low A factors are understandable in terms of the ordinary theory of absolute reaction rates. They show in the same manner that for reactions in solution the symmetrical decomposition of a polymer molecule should have an A factor of approximately 10^{13} , if the combination (or disproportionation) of two polymer radicals has an A factor of 10^{11} . This is in marked contrast to the behavior of ethane and butane discussed above. The reason for this is that the large polymer molecules and radicals cannot rotate freely but only librate or vibrate. Since these forms of motion are little affected by the size of the species there is no effect to correspond to the loss of rotational entropy in the case of the combination of two small radicals.

The author wishes to thank Professor M. G. Evans and Dr. M. Szwarc for numerous discussions.

¹⁴ T. Carrington and N. R. Davidson, J. Chem. Phys. 19, 1313 (1951).

¹⁵ R. A. Harman and H. Eyring, J. Chem. Phys. 10, 557 (1942).

¹⁶ J. H. Baxendale and M. G. Evans, Trans. Faraday Soc. 43, 210 (1947).

Studies in energy transfer

III. The effect of added gases on the decomposition of *cyclobutane*

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(Communicated by M. Polanyi, F.R.S.—Received 21 March 1953)

The effect of the addition of hydrogen, helium, neon, argon, nitrogen, methane, water, benzotrifluoride, toluene and mesitylene on the first-order rate constant for the decomposition of *cyclobutane* at low pressures has been measured. The results are compared with those obtained for the same gases under similar conditions for the isomerization of *cyclopropane*.

INTRODUCTION

Genaux & Walters (1951) have shown that the decomposition of *cyclobutane* to ethylene is a first-order gas-phase reaction, whose rate is given by the Arrhenius equation

$$k = 10^{15.71} \exp (62800/RT).$$

Furthermore, Kern & Walters (1952) have shown that the rate of reaction is little affected by packing the reaction vessel or by the addition of chain inhibitors such as propylene, nitric oxide or toluene. They concluded that the reaction is a clean unimolecular decomposition whose rate constant falls off at low pressures because the rate of collisional energy transfer is insufficient to maintain the Maxwell-Boltzmann energy distribution in the face of the reaction. They also found that the addition of non-reactive gases tends to restore the low-pressure rate constant to the high-pressure value. Accordingly, we thought it interesting to measure the effect of various gases under the same conditions and with the same apparatus that we had used in the study of the analogous isomerization of *cyclopropane* at low pressures (Pritchard, Sowden & Trotman-Dickenson 1952, 1953, part II).

EXPERIMENTAL

Materials

The *cyclobutane* was kindly given to us by the National Research Council of Canada; the high purity of this sample had been confirmed both by low-temperature distillation and by mass-spectrographic analysis. The inert gases were prepared and purified as described in part II.

Apparatus and procedure

The rate of decomposition of *cyclobutane* alone at pressures above 1 cm was followed by pressure measurements on a simple manometer attached to the reaction vessel. The low-pressure experiments were carried out in an exactly similar manner to those with *cyclopropane*, which were described in part II. No change was made for the study of the effect of the high-boiling additives. However, it was necessary to alter the apparatus to study the effect of the non-condensable additives, because the ethylene formed in this reaction is more volatile than the propylene produced in the isomerization of *cyclopropane*. Now the reaction was arrested by pumping the contents of the reaction vessel through a two-stage mercury diffusion pump into a large backing volume. Then the *cyclobutane*-ethylene mixture was separated from the non-condensable foreign gas by circulation for about 15 min through a trap cooled by liquid nitrogen boiling under reduced pressure. Control runs with known ethylene-argon mixtures showed that this procedure was satisfactory. When the additive was methane care was taken that the temperature did not fall below 70°K.

The *cyclobutane*-ethylene mixture was analyzed on a Blacet-Leighton apparatus (Blacet & Leighton 1931) by absorbing the ethylene on a mercuric acetate bead (Pyke, Kahn & LeRoy 1947). Tests showed that the ethylene was completely absorbed within 5 min; no absorption of the *cyclobutane* could be detected. This method of following the reaction is very convenient, especially for studying the effect of additives at low pressures of *cyclobutane*; it is probably not as accurate for following the decomposition of pure *cyclobutane* as the method used by Kern & Walters (1952), who followed the pressure change during the reaction.

No evidence of any side reaction was found after the reaction vessel had been aged; no non-condensable gas was formed and, in a run taken to completion, the contents of the reaction vessel were completely absorbed by a mercuric acetate bead. Mass-spectrographic evidence for the absence of side reactions has been given by Kern & Walters (1952).

RESULTS

Experiments with cyclobutane alone

The rate of decomposition of *cyclobutane* at temperatures between 448.2 and 448.6°C was measured in the pressure range from 10 to 0.0057 cm. In this region the rate constant fell from 3.8×10^{-4} to $1.06 \times 10^{-4} \text{ s}^{-1}$. The results are presented in figure 1 as a plot of $\log_{10} k/k_{\infty}$ against the decadic logarithm of the pressure in centimetres. The value of k_{∞} was found by extrapolating a plot of k^{-1} against

p^{-1} to infinite pressure. Most of the runs were to approximately 25 % conversion, but no detectable difference in the rate constant was observed when runs were carried to 60 % conversion. Within the accuracy of our experiments this can be explained if the collisional efficiency of ethylene in maintaining the rate constant of the reaction is half that of *cyclobutane*.

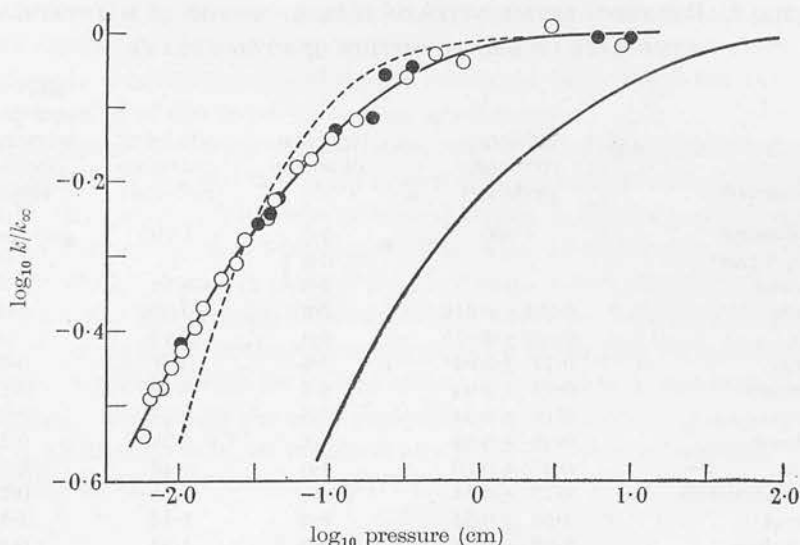


FIGURE 1. The dependence of the rate of decomposition of *cyclobutane* on pressure. O, runs to about 20 % conversion; ●, runs to about 50 % conversion; ---, calculated Hinshelwood curve; —, curve for *cyclopropane*.

Experiments with added gases

The experiments on the effect of added gases were carried out at *cyclobutane* pressures between 0.01 and 0.1 cm, a region in which the rate constant varies rapidly with pressure, and with pressures of additive between 0.2 and 1.0 cm. The typical results obtained for hydrogen are given in table 1, the final column of which shows the efficiency of hydrogen relative to *cyclobutane*, pressure for pressure, in maintaining the value of the rate constant. The results for all the

TABLE 1. THE EFFECT OF THE ADDITION OF HYDROGEN ON THE RATE OF DECOMPOSITION OF *CYCLOBUTANE*

temp. (°C)	<i>cyclobutane</i> pressure (cm)	hydrogen pressure (cm)	time (sec)	% conversion	$10^4 k$ (sec ⁻¹)	relative efficiency of hydrogen
448.1	0.040	0.60	1490	34.9	2.88	0.24
447.8	0.036	0.49	1690	37.6	2.79	0.31
447.9	0.043	0.62	1445	34.7	2.91	0.28
448.2	0.023	0.82	1931	44.6	3.06	0.27
448.3	0.039	0.69	1685	40.3	3.06	0.31

Efficiency of hydrogen relative to *cyclobutane* = 0.28 ± 0.03 (calculated on equivalent pressures).

additives studied are collected together in table 2. The choice of additive is severely restricted, not only because they must be both stable and unreactive at the working temperature, but also because they must be readily separable from the *cyclobutane-ethylene* mixture by low-temperature distillation. The errors quoted are the root-mean-square errors of five or six determinations.

TABLE 2. RELATIVE EFFICIENCIES OF FOREIGN BODIES IN MAINTAINING THE RATE OF DECOMPOSITION OF *CYCLOBUTANE*

molecule	efficiency (pressure/ pressure)	collision diameter (Å)	efficiency (collision/ collision)	efficiency in <i>cyclopropane</i> isomerization (collision/ collision)
<i>cyclobutane</i>	1.000	5.5	1.000	—
<i>cyclopropane</i>	—	5.0	—	1.000
ethylene	~ 0.50	4.5	~ 0.49	—
helium	0.096 ± 0.016	2.2	0.072	0.048
neon	0.097 ± 0.015	3.0	0.12	—
argon	0.17 ± 0.04	3.6	0.21	0.070
hydrogen	0.28 ± 0.03	2.7	0.10	0.12
nitrogen	0.18 ± 0.04	3.8	0.21	0.070
methane	0.50 ± 0.08	4.1	0.38	0.24
water	0.47 ± 0.10	4.0	0.44	0.74
benzotrifluoride	1.15 ± 0.14	8.5	0.85	0.75
toluene	1.50 ± 0.34	8.0	1.12	1.10
mesitylene	1.82 ± 0.34	9.0	1.23	0.89

DISCUSSION

The general shape of the curve for the decomposition of *cyclobutane* shown in figure 1 is as expected for a reaction whose rate falls at low pressures because the concentration of more energetic molecules is not being maintained. Moreover, this curve bears the expected relation to that for *cyclopropane* (shown by the solid line). No quantitative treatment of the *cyclobutane* decomposition has yet been reported, but the similar shape of the curve and its displacement to lower pressures are entirely in accord with the anticipated behaviour of a slightly more complex molecule.

For comparison, the curve derived from the simple Hinshelwood-Lindemann expression is shown by the dashed line. This expression predicts an incorrect shape for the curve, probably because the assumption that all molecules with energy in excess of the critical amount react at the same rate is inadequate.

There is some discrepancy between our results and those of Kern & Walters (1952) which might be caused by a 4°C difference in our temperature scales. Our six-junction chromel-alumel thermocouple was calibrated against the temperature of boiling sulphur and should not be in error by more than ± 0.3°C, which is about the accuracy of the thermocouple used by Kern & Walters. It is not a simple matter to determine accurately the mean temperature of large Pyrex reaction vessels, but we do not think that we could have estimated our temperature 4°C too high, for the temperature in the reaction vessel did not vary by

more than 0.5°C between the centre and the ends. However, for our present purpose the discrepancy is not serious because the shape of the plot of $\log k/k_{\infty}$ against $\log p$ does not vary appreciably with temperature changes of the order of 20°C .

In table 2 are shown the efficiencies of the gases relative to *cyclobutane* expressed in terms of collisions (the collision diameters used in these calculations are given in the table). The figures run closely parallel to those obtained with *cyclopropane*, and the conclusion that all large molecules cause deactivation on every collision is reinforced. Our present knowledge of collisional processes is too restricted for useful discussion of the minor variations in efficiency.

The intramolecular mechanism of the decomposition of *cyclobutane* is not known, but a consideration of the thermochemistry of the process is interesting. The heat of combustion has recently been measured (Coops & Kaarsemaker 1950) giving a ΔH for formation of 6.3 kcal/mole. The heat of formation of *n*-butane is -29.8 kcal/mole (Prosen & Rossini 1945), and the assumption of approximately 100 kcal each for the primary C—H dissociation energies (cf. Mortimer, Pritchard & Skinner 1952) leads to the value ΔH_f ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$) = 66 kcal. Hence the energy required for simple carbon-carbon bond fission in *cyclobutane* is about 60 kcal/mole. Essentially the same conclusion may be derived by considering that the heat of formation of an idealized strainless *cyclobutane* molecule would be approximately four CH_2 increments (Prosen & Rossini 1945), i.e. about

$$-(4 \times 4.9) = -19.6 \text{ kcal/mole.}$$

Hence, there is approximately 26 kcal/mole strain energy in *cyclobutane*, and if the normal carbon-carbon bond energy is 85 kcal, then the minimum energy required for simple bond fission in *cyclobutane* is $85 - 26 = 59$ kcal/mole; the experimental activation energy is 62.8 kcal.

Similar arguments based on the ΔH of formation of *cyclopropane* of 12.7 kcal/mole (Knowlton & Rossini 1949) lead to the value of about 59 kcal for the simple carbon-carbon bond fission to give a trimethylene radical, whereas the experimental activation energy is 65 kcal/mole. Crude calculations using a carbon-carbon bond of 85 kcal having a force constant of 4.5×10^5 dynes/cm (Crawford & Brinkley 1941) and allowing for the variation of strain energy with configuration (calibrated at C—C—C bond angles of 0, 60, 90, 108 and 120° from the heats of formation of ethylene, *cyclopropane*, etc.) show that the activation energy for the simple bond fission is not likely to be greater than the endothermicity.

However, there is some evidence that the trimethylene diradical is not involved in the reaction; Slater (1953), assuming that the transition state is determined by the approach of a hydrogen atom attached to one carbon atom to within a critical distance of an adjacent carbon atom, has explained the high frequency factor of this reaction ($10^{15.2}$), and predicted its quasi-unimolecular behaviour in excellent agreement with the experimental results. According to Slater's treatment, if the first step in the reaction is a carbon-carbon bond fission, the molecule may be regarded virtually as a triatomic molecule, and in this case the rate would have fallen off to a small fraction of its high-pressure value at these pressures; thus, if

the bond fission reaction has a frequency factor of about 10^{13} , as seems reasonable, the combined effect of the falling off and the lower frequency factor might be expected to outweigh the effect of the lower activation energy and reduce its rate to insignificant proportions compared with the other mechanism. Furthermore, it is difficult to see how the cleanliness of the reaction could be maintained in the presence of such molecules as methane, toluene and mesitylene if free radicals were involved.

If this is the case for *cyclopropane*, we might suspect with *cyclobutane*, despite the close agreement between the energy required for carbon-carbon bond fission and the experimental activation energy, that the reaction does not proceed in this way. A plausible mechanism is that two sides of the square formed by the four carbon atoms contract, while the other two stretch until two ethylene molecules separate. In this case, since the fission into two dimethylene radicals would require about 144 kcal ($2 \times 85 - 26$), the two shortened sides of the square, which are the latent ethylene molecules, must possess very considerable double-bond character in the transition state. Some evidence for this mechanism lies in the high frequency factor of this reaction ($10^{15.7}$) which may be explained by an increase in entropy due to the greater freedom of movement (possibly nearly free rotation) of the latent ethylene molecules in the transition state.

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Studies in energy transfer

II. The isomerization of *cyclopropane*—a quasi-unimolecular reaction

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(Communicated by M. G. Evans,* F.R.S.—Received 14 January 1953)

The thermal isomerization of *cyclopropane* to propylene is a homogeneous unimolecular reaction at 490° C and at pressures down of 0.007 cm. The rate constant of the unimolecular reaction falls off by a factor of ten as the pressure in the reaction system is decreased from 8.4 to 0.007 cm. The results are compared with various theories of quasi-unimolecular reactions.

The addition of a non-reacting gas to the system counteracts the falling off. The relative efficiencies of a number of gases for maintaining the unimolecular rate constant have been measured.

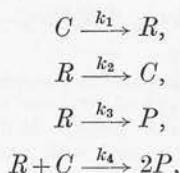
One of the methods of obtaining information on the collisional transfer of energy between molecules in the gas phase is the study of the dependence of the rate of unimolecular reactions on pressure. The principle of this method is straightforward and may be briefly stated. The rate of reaction of a particular molecule is a function of its energy content alone. The number of molecules, in a system at equilibrium, containing a particular amount of energy is given by the Maxwell-Boltzmann distribution. This equilibrium distribution is maintained by collisional energy transfer. The overall observed rate of the unimolecular reaction may be expressed as the sum of the products of the number of molecules in a given energy level multiplied by the specific rate constant for the reaction of a molecule in that level. Now, at low pressure the rate of energy transfer by collision may not be sufficiently rapid to maintain the Maxwell-Boltzmann distribution in the face of the reaction of the most energetic molecules. This depopulation of the higher energy levels results in the decline of the overall rate constant. Hence if a suitable expression can be found for the specific rate constants of molecules with particular energy contents, much information on the rate of energy transfer on collision may be gained. There are a number of treatments of this point which we shall consider more fully in the discussion in connexion with our results.

A prerequisite for this approach is the discovery of a suitable reaction in which only one molecule is involved in the chemical change and which may be studied conveniently and accurately over a very large range of pressures and which involves comparatively simple molecules containing not more than a dozen or so atoms. Most of the large number of investigations which have been made can be faulted on these points. Indeed, Pease (1942) considered that no reaction had yet been discovered, with the possible exception of the isomerization of *cyclopropane*,

* Professor Evans had agreed to communicate this paper before his death on 25 December 1952.

which fulfilled the necessary conditions for a satisfactory test of the theory to be made.

The thermal isomerization of *cyclopropane* was first studied from this point of view by Chambers & Kistiakowsky (1934). Their observations only covered the range from 1 to 100 cm pressure, but did indicate a decline in the rate constant of a factor of 1.4 in that region. They concluded that this was a genuine example of quasi-unimolecular behaviour, but Corner & Pease (1945) showed that the results, together with more data in the same pressure range obtained by them, could be equally well explained on the basis of a simple three-stage mechanism,



where *C* represents *cyclopropane*, *R* the trimethylene biradical and *P* propylene. One feature of this mechanism is that added non-reacting gases should have no effect upon the first-order rate constant, whereas they should increase the rate of a quasi-unimolecular reaction. Accordingly in support of their theory Corner & Pease pointed out that the addition of hydrogen had no effect upon the rate constant. However, as will be seen the effective pressure of hydrogen added relative to that of *cyclopropane* was so low that the effect would be within the experimental error, which was rather large. Furthermore, there is no evidence for the existence of radicals in the system. Using the steady-state approximation, Corner & Pease deduced an expression for the first-order rate constant k_1 from results if $k_3/(k_2 + k_3) = 0.88$ and $k_3 = 12k_4$ and from the results of Chambers & Kistiakowsky if $k_3/(k_2 + k_3) = 0.34$ and $k_3 = 12k_4$. (There appears to be an arithmetical error in their working here, for the recommended values of $k_3/(k_2 + k_3)$ and k_3/k_4 do not give a constant value for k_1 when taken in conjunction with Chambers & Kistiakowsky's results. Furthermore, the values of k_1 given in their paper as deduced from the work of Chambers & Kistiakowsky differ greatly from those deduced from their own work despite the fact that the experimental observations were concordant. However, if $k_3/(k_2 + k_3)$ is taken as 0.60 the results of Chambers & Kistiakowsky may be recalculated to give a constant value of k_1 in excellent agreement with that derived from Corner & Pease's experiments.) There is one critical feature of Corner & Pease's mechanism, in that it predicts that at sufficiently low, as at sufficiently high, pressures, the observed first-order rate constant should become independent of pressure. Taking their parameters we find that at low pressures the logarithm of the ratio of the first-order rate constant, k , to the rate constant at high pressure, k_∞ , should approach the value -0.80 . We have followed the reaction down to values of $\log_{10} k/k_\infty$ below -1.0 at which there is no sign that the ratio is tending to a constant value. This fact, taken in conjunction with the effect of added gases at high relative effective pressures observed by us and described in the experimental part of this paper, leads us to reject the mechanism of Corner & Pease as quite unsatisfactory.

The experimental part of this paper describes the extension of the measurements of the rate of thermal isomerization of *cyclopropane* to a new low-pressure range and the effect of added gases on the rate constant in this range. This extension of the range was made possible by the adoption of an improved technique for analyzing the very small quantities of gases involved at the lowest pressures.

EXPERIMENTAL

Materials

The *cyclopropane* was an I.C.I. product of B.P. anaesthetic quality; a batch analysis showed that 99.6 % of the gas was absorbed by concentrated sulphuric acid, and that less than 0.06 % of propylene was present. Mass-spectrometer analysis showed that no more than 0.01 % of propane could be present. The *cyclopropane* was carefully degassed before use.

Hydrogen was purified by passing it through a palladium thimble. Helium, argon, nitrogen and methane were commercially pure samples, further purified by contact with a sodium mirror. Carbon monoxide was prepared from anhydrous formic acid and concentrated sulphuric acid, and was also purified using a sodium mirror. The toluene was a highly purified sample; mesitylene was shaken twice with concentrated sulphuric acid, sodium carbonate solution and then water, and dried over calcium chloride; benzotrifluoride was washed with sodium hydroxide and water, dried with magnesium sulphate and distilled. Before being used, the liquids were degassed by bulb to bulb distillation *in vacuo*.

Apparatus and procedure

The reaction vessel was a cylindrical Pyrex bulb of 2 l. capacity, which was supported in a furnace thermostatically controlled at approximately 490° C. The main furnace element was wound on a cylindrical iron former, with provision for extra heating at the ends. The temperature was maintained constant by a gas thermometer which controlled a subsidiary heater winding (Taylor & Sickman 1932). The gas thermometer consisted of a Pyrex Dewar flask, which was a close fit round the reaction vessel, the subsidiary heater winding being wound directly on the outside of the flask. The annular space contained air under about 120 cm pressure, and was connected by capillary tubing to a mercury contact manometer which operated the secondary heater winding through an electronic relay. By adjusting the amount of air in the annular space, any convenient temperature could be maintained. Using this arrangement, the temperature of the reaction vessel measured with a standardized six-junction chromel-alumel thermocouple, could be maintained constant to within $\pm 0.04^\circ \text{C}$; the temperature variation along the length of the reaction vessel was less than $\pm 0.5^\circ \text{C}$.

The *cyclopropane* and the added gas were introduced into the reaction vessel through capillaries from a pair of calibrated gas burettes; this process took from 10 to 20 s, for which a slight correction was applied; each gas burette was isolated from the reaction vessel by a mercury-sealed magnetic cut-off. In those cases when the second body being studied was a liquid, the vapour was bled into the

reaction vessel until the required pressure, as indicated on a modified Pearson manometer (Pearson 1931), was reached. In all experiments where second bodies were used, the *cyclopropane* was introduced into the reaction vessel first, to exclude mixing difficulties, since the pressure of foreign gas used was always considerably higher than the pressure of *cyclopropane*; otherwise, the greater portion of the *cyclopropane* would tend to remain in the dead space, and not enter the reaction vessel.

At the end of a run, the contents of the reaction vessel were admitted to two wide-bore traps cooled in liquid nitrogen, any non-condensable foreign gas, if added, being pumped away at the same time. Since the reaction was arrested in this way, the connexion from the reaction vessel to the analysis section was made of wide-bore tubing, through a mercury float-valve cut-off constructed from 18 mm diameter tubing. This was done so that the gas should flow from the reaction vessel in a time which was short compared with the length of the runs even at the lowest pressures used; the results had to be corrected by 2 % to allow for the rather large dead space thus introduced. In those cases where the second body was not a permanent gas, the *cyclopropane*-propylene mixture was separated off by low-temperature fractionation at this juncture. The *cyclopropane*-propylene mixture was then passed through a mercury float-valve cut-off into a small trap, and samples were transferred to the gas-holders of a Blacet-Leighton micro-analysis apparatus (Blacet & Leighton 1931) using a Toepler pump.

The propylene was absorbed on a mercuric acetate bead, as recommended by Pyke, Kahn & LeRoy (1947). Tests showed that while the propylene was completely absorbed within 5 min, there was only a very small absorption of *cyclopropane*, amounting to less than 0.5 % of the sample. This uncertainty only becomes serious in runs going to high conversions, for the rate constant is then very sensitive to the accuracy of the analysis; most runs were carried to about 35 % conversion, although some were continued to conversions as high as 70 % to test the unimolecularity of the reaction. When large quantities of product were available, considerable care was taken to obtain a representative sample for analysis, because a slight fractionation of the *cyclopropane*-propylene mixture during the low-temperature distillations was observed in the early runs carried out at higher pressures. In no case did the reactants or the products come into contact with a greased tap from the time they were measured out to the end of the analysis, thereby eliminating the possibility of incurring any loss of materials. The calculated rate constants represent the mean of either two or three separate micro-analyses for each run at all but the very lowest pressures.

Experiments were carried out to ensure that there were no side reactions of any importance. Tests showed that no non-condensable gases were produced in the reaction, and that no condensation took place. For C_3 hydrocarbons, this is a rigorous test, since side reactions must lead either to condensation or to lower hydrocarbons which are permanent gases. In the early experiments, condensation was observed in the runs immediately following the admission of air to the reaction vessel, but when this had been realized, the vessel was always 'aged' by leaving *cyclopropane* in it overnight, after which no appreciable loss could be detected.

RESULTS

Experiments with cyclopropane alone

Experiments using *cyclopropane* alone were carried out at pressures ranging from 8.41 to 0.0067 cm of mercury, the rate constant falling from $3.15 \times 10^{-4} \text{ s}^{-1}$ to $3.19 \times 10^{-5} \text{ s}^{-1}$. The results of these measurements, together with those of Chambers & Kistiakowsky (1934), are presented in figure 1 as a plot of $\log_{10} k/k_{\infty}$ against the decadic logarithm of the *cyclopropane* pressure in cm, where (Chambers & Kistiakowsky 1934)

$$\log_{10} k_{\infty} = 15.17 - 65000/2.3RT.$$

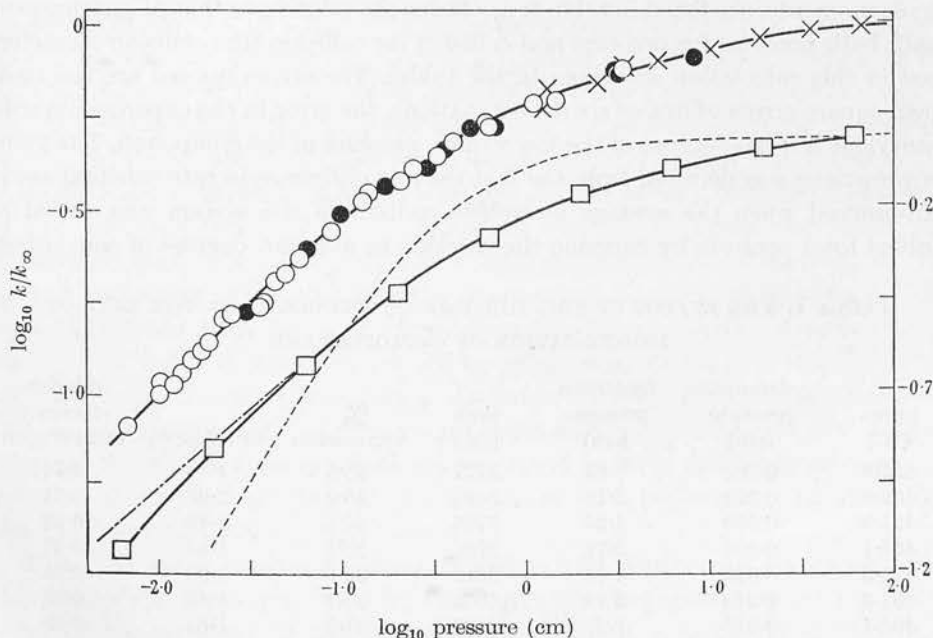


FIGURE 1. The dependence of the rate of isomerization of *cyclopropane* on pressure. Upper curve: \circ , runs to about 30 % conversion; \bullet , runs to about 70 % conversion; \times , results of Chambers & Kistiakowsky. Lower curves: —, experimental results displaced by 0.3 log units; ----, calculated Hinshelwood curve; - · - · -, calculated Kassel curve; \square , points calculated by Slater.

This value is in excellent agreement with the value obtained by extrapolating a plot of k^{-1} against p^{-1} to infinite pressure for our own results; this concordance must be largely fortuitous, since Chambers & Kistiakowsky imply that their temperature scale may be in error by as much as 2° C ($\pm 12\%$ in k_{∞}), and although we took considerable care to arrive at the best value for the temperature of the gas in our reaction vessel, an absolute error of as much as 1° C cannot be definitely ruled out. The points in figure 1 represent runs carried out at near 491° C ; a number of experiments carried out for selected pressures at 470° C showed that the variation in the ratio of k/k_{∞} was not sensitive to temperature.

Experiments with added gases

Experiments in which added gases were used were carried out for *cyclopropane* pressures of from 0.01 to 0.1 cm, a region where the rate constant shows considerable falling off, and for various pressures of additive. The choice of additive was restricted by two important requirements, first that the substance should be stable at the temperature of the experiment, and secondly that it should be readily separable from the *cyclopropane*-propylene mixture by low-temperature distillation. The results for hydrogen are given in table 1, the final column representing the efficiency of hydrogen relative to *cyclopropane*, pressure for pressure, in maintaining the value of the rate constant. The results obtained for a series of additives, representing a wide variation in collision diameters, vibrational frequencies and dipole moments, are listed in table 2, as efficiencies relative to that of *cyclopropane* itself, both pressure for pressure and collision for collision (the collision diameters used in this calculation are given in the table). The errors quoted are the root-mean-square errors of five or six determinations, the error in the experiments with mesitylene is large because of the low vapour pressure of the compound. The value for propylene was deduced from the fact that no difference in rate constant could be observed when the average propylene content of the system was varied at a given total pressure by carrying the reaction to different degrees of conversion.

TABLE 1. THE EFFECT OF THE ADDITION OF HYDROGEN ON THE RATE OF ISOMERIZATION OF *CYCLOPROPANE*

temp. (°C)	<i>cyclopropane</i> pressure (cm)	hydrogen pressure (cm)	time (sec)	% conversion	$10^4 k$ (sec ⁻¹)	relative efficiency of hydrogen
492.6	0.098	0.93	2727	38.8	1.80	0.24
492.8	0.071	2.19	2494	40.5	2.08	0.21
493.5	0.078	3.25	2726	48.1	2.40	0.22
491.1	0.026	0.71	2704	32.5	1.45	0.27
491.3	0.025	1.91	2312	35.5	1.90	0.24
491.4	0.018	0.43	3665	37.1	1.26	0.26
492.1	0.017	1.27	2286	31.9	1.68	0.20
491.7	0.020	3.14	2107	38.1	2.28	0.29

Efficiency of hydrogen relative to *cyclopropane* = 0.24 ± 0.03 (calculated on equivalent pressures).

At high pressures it has been found that the rate of isomerization is unaffected by packing the reaction vessel. The reproducibility of the relative efficiencies of hydrogen, as recorded in table 1, and of other added gases over a wide range of pressure *cyclopropane* and added gas indicates that no heterogeneous reaction is occurring at the lowest pressures.

DISCUSSION

In figure 1 we have compared our experimental results with the predictions of three closely related theories of unimolecular reaction. The first is the original Hinshelwood-Lindemann (Hinshelwood 1940) theory in which no allowance is made for the possibility that molecules containing energy (E) in excess of the

minimum critical energy (E_0) for reaction will have specific rate constants greater than those with only the minimum energy content. The marked divergence of the dotted curve, computed for a molecule of 5 Å collision diameter and with energy content distributed among 11 square terms, from the solid curve shows that the assumption made is oversimplified. The more complex the molecule the more unsatisfactory this assumption will become.

The second theory tested is the classical form of the theory due to Kassel (1932) in which the observed unimolecular rate constant is given by the expression,

$$\frac{k}{k_\infty} = \frac{1}{(N-1)!} \int_0^\infty \frac{x^{N-1} e^{-x} dx}{1 + \frac{A}{Z} \left(\frac{x}{b+x} \right)^{N-1}},$$

where $b = E_0/kT$, $x = (E - E_0)/kT$, A is the pre-exponential factor in the Arrhenius equation, N is the number of effective oscillators in the molecule and Z is the collision frequency. The number of effective oscillators can be chosen at will to give the best possible fit between the theoretical and experimental curves with the proviso that N should not exceed $3a - 6$, which is the number of vibrational modes of a non-linear molecule containing a atoms. As it is usually considered that N is of the order of one-half of $3a - 6$, this is not a serious or useful restriction. The theories of Rice & Ramsperger (Kassel 1932) give very similar expressions. The dashed curve was obtained (following Chambers & Kistiakowsky) using $N = 13$, $E_0 = 65$ kcal and 3.9 Å for the collision diameter of cyclopropane. A more convex curve which would be a better fit would be obtained by taking $N = 12$ and a corresponding larger value for the collision diameter. As the calculations are laborious this was not done because the important point had been established that a treatment of the Kassel type in which an allowance is made for the greater rate of reaction of the more energetic molecules, was a much better approximation than the Hinshelwood-Lindemann treatment.

Slater (1953) has made a considerable advance by producing a theory by which it is possible to define precisely the number of effective oscillators given a knowledge of the structure of the molecule. In addition, a complete spectroscopic vibrational analysis of the molecule is necessary for the application of the theory which is fully described by Slater (1953). The points are plotted as squares in figure 1 from the expression, which is closely related to that of Kassel,

$$\frac{k}{k_\infty} = \frac{1}{\Gamma\left(\frac{n+1}{2}\right)} \int_0^\infty \frac{x^{\frac{1}{2}(n-1)} e^{-x} dx}{1 + \frac{\theta}{x^{\frac{1}{2}(n-1)}}},$$

where n is the effective number of non-degenerate vibrational modes in the molecule, for cyclopropane $n = 13$, $\theta = 3.6Z\beta/A$, $\beta = \Gamma\left(\frac{n+1}{2}\right) \mu_1 \mu_2 \dots \mu_n (4\pi b)^{\frac{1}{2}(n-1)}$ and μ_s is a dimensionless parameter characteristic of the vibrational properties of the molecule; its derivation is fully discussed in Slater's paper. The factor 3.6 in the expression for θ has been introduced arbitrarily as a shift in the log p axis to make the theoretical and experimental curves coincide when the collision diameter of cyclopropane is taken as 5.0 Å. The important point, however, which seems to be

established is that the theory which involves no arbitrary parameters at all, predicts with a high degree of accuracy the shape of the curve of $\log k/k_\infty$ against $\log p$.

Howlett (1952) has attempted to discriminate between the Hinshelwood-Lindemann and Rice-Ramsperger theories in rather the same manner as is done here using the dehydrochlorination of 1:1-dichloroethane as a test case. His arguments, however, are not convincing. In his figure 3 he shows a plot which is similar to our figure 1, wherein he plots his experimental points and smoothed curve together with points (series B) calculated from the Hinshelwood-Lindemann expression

$$k/k_\infty = 1/(1 + 6.87/p),$$

where p is the pressure in mm of mercury, and points (series A) calculated from the Rice-Ramsperger expression. The points of series A admittedly fall much closer to the experimental curve than do those of series B, which he claims shows that the Rice-Ramsperger theory gives a truer explanation of the facts than that of Hinshelwood & Lindemann. But this comparison is not fair because the points which may be calculated from the Hinshelwood-Lindemann expression,

$$k/k_\infty = 1/(1 + 1.3/p),$$

fit the experimental results quite as well as the points of series A. Since the constant β in the expression $k/k_\infty = 1/(1 + \beta/p)$

is always adjusted to fit the experimental points, this formula is quite as acceptable as that chosen by Howlett. In fact, the fit of the Hinshelwood-Lindemann plot is so good that it may be doubted if the reaction is as simple as it is claimed to be. Furthermore, the points which may be calculated in series A for k at 15 and 20 mm which Howlett does not plot fall rather badly off the experimental curve. The most reasonable conclusion seems to be that, allowing for the scatter of the experimental points, there is little to choose between the two theories. Lastly, it may be pointed out that it is very difficult to decide between the theories of unimolecular reaction when the range of k/k_∞ observed only lies between unity and one-third, unless the experimental work is of extremely high accuracy.

One of the principal uncertainties in applying any of the theories of unimolecular reactions is that the collision diameter for which a numerical value must be selected

TABLE 2. RELATIVE EFFICIENCIES OF FOREIGN BODIES IN MAINTAINING THE RATE OF ISOMERIZATION OF CYCLOPROPANE

molecule	efficiency (pressure/pressure)	collision diameter (Å)	efficiency (collision/collision)
cyclopropane	1.000	5.0	1.000
helium	0.060 ± 0.011	2.2	0.048
argon	0.053 ± 0.007	3.6	0.070
hydrogen	0.24 ± 0.03	2.7	0.12
nitrogen	0.060 ± 0.003	3.8	0.070
carbon monoxide	0.072 ± 0.009	3.8	0.084
methane	0.27 ± 0.03	4.1	0.24
water	0.79 ± 0.11	4.0	0.74
propylene	~ 1.0	5.0	~ 1.0
benzotrifluoride	1.09 ± 0.13	8.5	0.75
toluene	1.59 ± 0.13	8.0	1.10
mesitylene	1.43 ± 0.26	9.0	0.89

is an unknown quantity. Usually a value corresponding to the gas kinetic collision diameter is used, but it is by no means certain that every gas kinetic collision results in the transfer of internal energy. In most cases it is impossible to obtain direct evidence on this point; however, some information can be gleaned from the values of the relative efficiencies of the various gases recorded in table 2. The efficiencies calculated on a pressure basis are directly determined, but it seems that efficiencies based upon the number of gas kinetic collisions between the various types of molecule will be more illuminating; accordingly, we have tabulated these efficiencies in the last column. No statistical correction was made to allow for counting all collisions between the like *cyclopropane* molecules twice because here we are not concerned with collisions between like molecules, but with collisions between the relatively few energized *cyclopropane* molecules and the rest of the molecules in the system. The reasonable assumption is made that the collision diameters of the energized molecules are the same as those of the ordinary molecules. It can be seen that the simpler molecules have efficiencies considerably less than that of *cyclopropane* but that all the more complex molecules have similar efficiencies. The simplest interpretation of this fact is that significant internal energy transfer occurs between the energized *cyclopropane* molecule and another complex molecule on every collision but less often when the collision is with a small and simple molecule. The usual assumption of the theories, therefore, receives some confirmation from our results. This is the first evidence on this point which has been obtained and is therefore, of some importance. We hope to be able to find out whether the same order and magnitude of the efficiencies occur for other reactions.

The efficiencies found for the added gases have another and more practical interest. Several of the gases studied have been used as carrier gases in flow pyrolyses. When pyrolyzing simple molecules with a comparatively small number of internal vibrations it is quite possible that the pressure in the system, usually about 5 to 20 mm, is so low that the Maxwell-Boltzmann distribution of energy is not maintained. Then the rate of energy transfer may become the rate-determining factor in the reaction. Toluene appears to be capable of transferring energy by collision far more efficiently than say nitrogen, hydrogen or helium, which have also often been used as carriers, and consequently has great advantages as a carrier when the rate of thermal decomposition of small molecules is being investigated.

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792. *The Thermal Decomposition of Azomethane.*

By M. PAGE, H. O. PRITCHARD, and A. F. TROTMAN-DICKENSON.

The thermal decomposition of azomethane has been reinvestigated in the temperature range 390—450° by the "toluene-carrier" flow technique. The rate constant for the decomposition in 15 mm. of toluene is given by $k = 10^{14} e^{-46,000/RT}$ sec.⁻¹. The experiments provide strong evidence that the primary step in the decomposition is the splitting-off of a methyl radical. The reason for the discrepancy between these results and those obtained in static systems and the bond strengths in azomethane are discussed.

THE thermal decomposition of azomethane has been investigated by several workers (Schumacher, "Chemische Gasreaktionen," Steinkopf, Dresden, 1938) because there was good evidence that it is a unimolecular reaction whose rate is dependent on the overall pressure in the reaction system, at pressures which are readily accessible to experiment. It has frequently been supposed that the azomethane molecule splits directly into an ethane and a nitrogen molecule, but this view receives no support from Riblett and Rubin (*J. Amer. Chem. Soc.*, 1937, **59**, 1537) who analysed the products formed in the decomposition and found considerable quantities of methane, some ethylene, and some unidentified involatile products. There are very few undoubtedly unimolecular reactions whose rates have been found to depend on the overall pressure and it is important to know if the decomposition of azomethane occurs so simply that it may be used to test theories of unimolecular reactions and of energy transfer.

There is a second point of interest in connection with this reaction: the rate constant has been given as $k = 3.1 \times 10^{16} \exp(-52,000/RT)$ sec.⁻¹ (Ramsperger, *ibid.*, 1927, **49**, 912; Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932) and alternatively as $k = 8 \times 10^{15} \exp(-50,200/RT)$ (Rice and Sickman, *J. Chem. Phys.*, 1936, **4**, 242); in either case the pre-exponential or *A* factor is very much larger than that which has been considered "normal" on theoretical grounds. It is understandable that such high *A* factors should be found for chain reactions and it has been suggested that this reaction is a chain decomposition.

By studying the decomposition in a flow system in the presence of toluene we hoped to isolate the initial step of the azomethane decomposition and so throw light on these matters.

EXPERIMENTAL

Materials.—*NN'*-Dimethylhydrazine dihydrochloride (Hatt, *Org. Synth.*, 1936, **16**, 18) was converted into the cuprous chloride addition compound of azomethane (Diels and Koll, *Annalen*, 1925, **443**, 262) which when heated at 120—140° yielded azomethane; the gas was purified by bulb-to-bulb distillation in a vacuum-system. The toluene was twice pyrolysed and distilled before it was used for kinetic experiments.

Apparatus.—This was of the type used by Sehon and Szwarc (*Proc. Roy. Soc.*, 1950, *A*, **202**, 263).

Procedure.—The products of the pyrolysis flowed through an ice-salt trap which removed the dibenzyl, then through liquid-nitrogen traps which removed the condensable products; the methane and nitrogen were pumped into a storage and analytical system. The proportion of methane in the non-condensable gases was found by burning the mixture in oxygen over a platinum filament and measuring the carbon dioxide formed. As the analytical system was not very suitable for the determination of ethane the amount formed was taken as equal to ($N_2 - \frac{1}{2}CH_4$). Ethane was identified by its vapour pressure in the system.

The toluene pressure in the flow system varied between 11 and 16 mm., the toluene : azomethane ratio between 10 and 30, and the contact time was between 1.2 and 1.4 sec. Between 10 and 50% of the azomethane was decomposed in a run. In calculating the results in the usual way on the basis of the nitrogen formed in the decomposition it was assumed that azomethane obeyed the perfect-gas laws.

RESULTS AND DISCUSSION

A plot of the logarithms of the rate constants against the absolute temperature is shown in the Figure. The solid line corresponds to the Arrhenius equation, $k = 10^{14} \exp(-46,000/RT)$ sec.⁻¹. The amount of methane formed varied from 30% of the non-condensables at the lower temperatures to 50% at the higher. It must be supposed that all this methane is produced from methyl radicals released in the primary decomposition which abstract hydrogen atoms from the toluene carrier gas. The ethane found could be produced either by a partial initial split of the molecule into ethane and nitrogen or by the combination of methyl radicals. It is not possible to decide directly by which path it is formed but it can be shown that the rate of formation of ethane is such that it may readily be accounted for by the combination of methyl radicals present in the concentrations corresponding to the rate of production of methane. If the rate constant for the reaction of methyl radicals with toluene is given by $k = 1.4 \times 10^{11} \exp(-8300/RT)$ mole⁻¹ c.c. sec.⁻¹ (Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1951, 19, 329; Gomer and Kistiakowsky, *ibid.*, p. 85), then the concentration of methyl radicals in a typical experiment in the middle of the temperature range, at 417°, was 1.07×10^{-11} mole c.c.⁻¹ in the reaction zone. This corresponds to a rate of formation of ethane of 5.73×10^{-9} mole c.c.⁻¹ sec.⁻¹, which may be compared with the observed rate of 3.2×10^{-9} mole c.c.⁻¹ sec.⁻¹. This is certainly of the correct order of magnitude and the difference probably arises partly because the effective volume of the reactor for the reactions of methyl radicals is rather larger than the effective volume for the decomposition. The positions of the limits of the reaction zone are determined by the temperature profile in the furnace and consequently will be rather further from the hottest region for reactions with low activation energies. Because of this uncertainty and because the experimental errors in the determination of the methane : ethane ratio are rather large, a reliable value for the rate of reaction of methyl radicals with toluene cannot be calculated from our results, but the findings are strong evidence that all the ethane comes from the combination of methyl radicals.

Our results are compared with those of other workers and this is done in the Figure. The points for 15 mm. total pressure are taken from the smoothed curves obtained by the authors for the variation of rate constant with pressure at the different temperatures. It has been assumed that toluene and azomethane have approximately equal efficiencies for purposes of energy transfer; this has not been proved for azomethane but the efficiencies are very similar for toluene, and indeed all large molecules, with cyclopropane (Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, A, 217, 563) and cyclobutane (*idem, ibid.*, 218, 416). The agreement between the three sets of results is excellent.

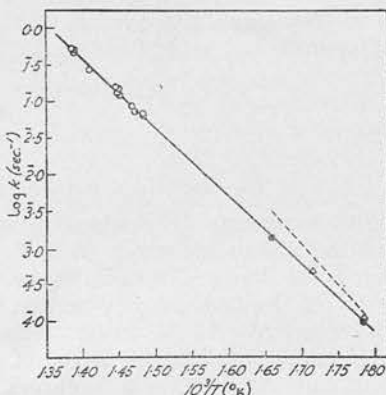
A reason may be suggested for the discrepancy between these results and those obtained at high pressures, and for the complexity of the products from pure azomethane. The near identity of the rates measured by us and those obtained by the workers in static systems suggests that the same process, which is the fission of a C-N bond, is rate-determining in each case. In pure azomethane, the methyl radicals will abstract hydrogen atoms from the substrate and will combine with the Me·N·N·CH₂· radicals so formed. Ethyl radicals, and hence ethylene, may be formed by the subsequent decomposition of C₂H₅·N·NMe; the high-boiling products are probably formed by the addition of radicals to the nitrogen double bond (Taylor and Jahn, *J. Chem. Phys.*, 1939, 7, 474). The higher activation energy found at high pressures is probably caused by the decomposition of some of the Me·N·N·CH₂· radicals which are formed in greater numbers at high pressures. The rate of decomposition of this chain-carrying radical will be markedly temperature-dependent. The number decomposing cannot be large as the quantum yield for the photolysis

of azomethane is only slightly dependent upon temperature (Burton, Davis, and Taylor, *J. Amer. Chem. Soc.*, 1937, **59**, 1989). This decomposition will explain the high activation energies which lead to the abnormal frequency factors.

The activation energy of a unimolecular reaction whose rate is a function of pressure is also dependent on pressure, but the dependence is not sufficiently marked to be the cause of the difference found here (Slater, *Phil. Trans.*, 1953, **246**, A, 57). Probably the best expression for the high-pressure rate constant is $k = 1.5 \times 10^{14} \exp(-46,000/RT)$ sec.⁻¹. In view of these results it seems that the dependence of the rate constants on pressure is real but that the shape of the pressure-rate-constant curve is influenced by factors other than energy transfer. Consequently this decomposition is not an ideal reaction on which to test theories of unimolecular reactions.

Arrhenius plot for the decomposition of azomethane in a system at approx. 15 mm. total pressure.

- This work.
- Ramsperger (*loc. cit.*).
- △ Sickman and Rice (*loc. cit.*).
- Ramsperger's results (*loc. cit.*) at infinite pressure.



The heat of formation of azomethane is not known, but the heat of combustion of azoisopropane, $\text{Pr}^i\text{N}:\text{N}:\text{Pr}^i$, has been found (Coates and Sutton, *J.*, 1948, 1187) to be $\Delta H_f(\text{Pr}^i\text{N}:\text{N}:\text{Pr}^i, \text{gas}) = 19.4 \pm 0.8$ kcal./mole. Comparison with the substitution heats for olefins ("Selected Values of Properties of Hydrocarbons," Nat. Bur. Stand., Circular No C461, Washington, 1947) leads to the value $\Delta H_f(\text{Me}^i\text{N}:\text{N}:\text{Me}^i, \text{gas}) = 43.2$ kcal./mole, an estimate which is unlikely to be in error by much more than ± 2 kcal./mole. If $\Delta H_f(\text{CH}_3, \text{gas}) = 32.6$ kcal. (Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220) is then used, this leads to a value of $D_1 + D_2$ (i.e., the heat of the process $\text{Me}^i\text{N}:\text{N}:\text{Me}^i \rightarrow \text{N}_2 + 2\text{Me}$) of 22 kcal./mole. Making the usual assumptions (Szwarc, *Chem. Reviews*, 1950, **47**, 75), we identify the activation energy of 46 kcal. with D_1 . The situation where D_1 is very much greater than D_2 exists in the alkylmercury series (Mortimer, Pritchard, and Skinner, *loc. cit.*), where, for example, $D_1 + D_2$ for HgMe_2 is 57 kcal., $D(\text{Me}-\text{HgMe})$ being 51 kcal./mole (Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, **A**, **218**, 269). Azomethane is the only known case in which D_1 is greater than $D_1 + D_2$; however, this extreme result is not entirely unexpected in view of the very large amount of energy required to raise the nitrogen molecule to a bivalent state from its zero-valent ground state. The lowest triplet state of N_2 is $A^3\Sigma_u^+$ which is 143.5 kcal. above the ground state (Herzberg, "Diatomic Molecules," Van Nostrand, New York, 1950) and it is reasonable to assume that the valency state is not far removed from this level. We can form an estimate of this excitation energy from the thermochemical data in the following way: the strength of a normal C-N single bond is approximately 83 kcal./mole (Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339), so that $D_1 + D_2$ for azomethane should be 166 kcal. if no excitation energy were regained by N_2 in returning to its zero-valent state; the actual value of $D_1 + D_2$ is 22 kcal., so that the excitation energy involved is $166 - 22 = 144$ kcal./mole, which is very close to the spectroscopic estimate, although this agreement is probably fortuitous.

It is possible that the molecule does not initially lose one methyl group closely followed by a second, but that both methyl groups split off simultaneously. It has hitherto not been necessary to postulate such a mechanism for any other reaction and it can be shown

by thermochemical argument that it is not necessary in this case either. Compare the bond strengths in the two analogous molecules



To the first approximation the Me-N dissociation energy in azomethane should be 83 kcal., and the Me-C dissociation energy in acetone should be 84 kcal. (Roberts and Skinner, *loc. cit.*); however, the C-C dissociation energy in acetone is only 73 kcal.; this weakening of 11 kcal. may be ascribed to a three-electron bond formed by conjugation of the free electron on the carbon atom with one of the lone pairs on the oxygen atom in the Me·CO· radical. That this resonance energy is of the correct order of magnitude may be seen from a study of the annexed Table, in which the relevant dissociation energies (in kcal./mole) are collected; they are all based on the values given by Gaydon ("Dissociation Energies," 2nd edn., Chapman and Hall, London, 1953) which, although they may not be correct,

Azomethane	Acetone
$D(-\text{N}=\text{N}-) = 82^a$	$D(>\text{C}:\text{O}) = 178^a$
$D(-\text{N}=\text{N}^+) = 201^b$	$D(\cdot\text{C}:\text{O}^+) = 194^b$
$D(\text{N}\equiv\text{N}) = 225^b$	$D(\text{C}\overline{\text{C}}\text{O}) = 256^b$

^a Thermochemical estimate.

^b From Gaydon, *op. cit.*

are internally consistent. The strengthening due to three-electron bond resonance in CO⁺ relative to >CO in acetone is 16 kcal., which is of the same order of magnitude as the stabilisation of the Me·CO· radical (the stabilisation of Me·CO· is about two-thirds of that in CO⁺). In the azomethane case, the stabilisation by three-electron bond resonance of N₂⁺ with respect to -N=N- in azomethane itself is 119 kcal. If again we take two-thirds of this as the stabilisation energy of the Me·N·N· radical, we get 80 kcal., leaving the dissociation energy $D(\text{Me}-\text{N}\cdot\text{N}\cdot\text{Me})$ of the order of 83 - 80 = 3 kcal./mole. This calculation merely serves to show that 46 kcal./mole is not an unreasonably low value for the dissociation energy of this single C-N bond: no significance should be ascribed to the exact calculated value.

The idea of this investigation was suggested during a discussion between one of the authors and Professors O. K. Rice and M. Szwarc.

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The Thermal Decomposition of tert.-Butylamine.

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[Reprint Order No. 4651.]

The thermal decomposition of *tert.*-butylamine has been studied in a static system in the temperature range 498—541° and over the pressure range 5—18 cm. The reaction was followed by pressure measurements and by analysis of the products. The pressure increase is due to the alternative simultaneous homogeneous first-order molecular scissions:



and



together with a subsequent slow reaction of the products, for which a correction can be readily applied. The ratio of ammonia to methane was $1:2.5 \pm 0.1$ over the temperature range studied, indicating that the activation energies of reactions (1) and (2) do not differ by more than 1 kcal./mole. A least-squares Arrhenius plot gave an overall rate constant

$$k = 10^{14.79} \exp(-67,100/RT) \text{ sec.}^{-1}.$$

A LARGE number of unimolecular decompositions are known in which one molecule splits directly into two normal molecules. These reactions may be called "molecular-split" reactions, to distinguish them from reactions in which free radicals are formed. The simplest reactions of this class are those which occur through a transition state containing a ring of four atoms and they are often called four-centre reactions. The activation energies of many of these reactions have been measured. In Table I are given the activation energies of some of the simplest of them (including the results of this research).

TABLE I. Activation energies (in kcal./mole) of reaction of the type
 $\text{CH}_3\text{CR}_2\text{X} \longrightarrow \text{CH}_2\text{CR}_2 + \text{HX}$.

CH ₃ CR ₂ X	HX				
	HCl	HBr	H ₂ O	NH ₃	CH ₄
EtX	60.8 ^a	53.9 ^d	—	—	—
PrX	50.5 ^b	47.8 ^d	—	—	—
BuX	41.4 ^c	42.2 ^d	65.5 ^e	67.1 ^f	59.3 ^g
Bu ^t NH ₂	—	—	—	67.1 ^f	67.1 ^f

^a Barton and Howlett, *J.*, 1949, 148. ^b Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114. ^c Barton and Onyon, *ibid.*, 1949, **45**, 725. ^d Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6220; Green, Harden, Maccoll, and Thomas, *J. Chem. Phys.*, 1953, **21**, 178. ^e Schultz and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395. ^f This work. ^g Peard, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1952, **A**, **214**, 330.

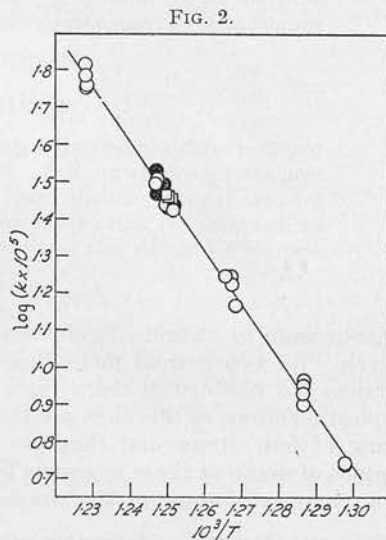
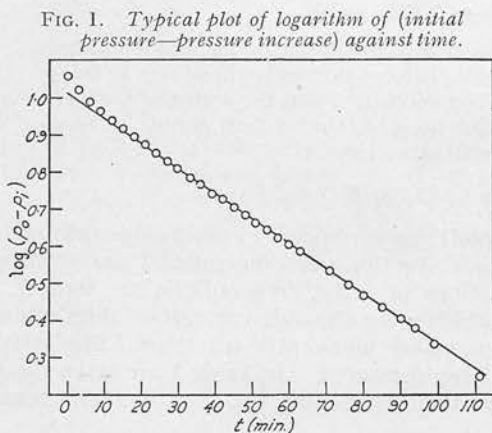
However, no satisfactory interpretation of the variations in their activation energies has yet been given. In an attempt to throw light on the general theoretical problem by provision of further results the decompositions of ethanethiol and isobutanethiol (2-methylpropane-2-thiol) were examined. Our experimental results with the former are exactly similar to those of Trenner and H. A. Taylor (*J. Chem. Phys.*, 1933, **1**, 77), though we regard their mechanism involving the initial formation of polysulphides as rather improbable since the sulphur-sulphur bond is not strong. Very similar results were found by us with isobutanethiol so that it was not suitable for the present purpose either. This was disappointing, as a consideration of the bond strengths might lead one to suppose that the behaviour of the alkanethiols would be similar to that of the alkyl chlorides and bromides. The decomposition of *tert.*-butylamine was expected to occur smoothly because

of its similarity to *tert.*-butanol. It was found that *tert.*-butylamine decomposed by way of the two molecular-split mechanisms (1) and (2) (above), having rate constants given respectively by the expressions $k_1 = 1.7 \times 10^{14} \exp(-67,000/RT) \text{ sec.}^{-1}$ and $k_2 = 4.4 \times 10^{14} \exp(-67,000/RT) \text{ sec.}^{-1}$. This is of interest because examples of a molecule reacting by two distinct molecular-split mechanisms are rare, though of course, numerous reactions are known which proceed by different ionic or free-radical mechanisms.

However, this work has complicated rather than clarified the general problem of the factors affecting the activation energy of molecular-split reactions.

EXPERIMENTAL AND RESULTS

Materials.—*tert.*-Butylamine (B.D.H.), distilled through a 30-plate column (reflux ratio 8:1), had b. p. $64.2^\circ/757 \text{ mm}$. The toluene was a highly purified sample. Before use the reagents were carefully degassed by bulb-to-bulb distillation *in vacuo*.



Arrhenius plot of results:

- Runs in unpacked vessel.
- Runs in packed vessel.
- Runs with toluene.

Apparatus and Procedure.—The reaction vessel was a 2-l. Pyrex bulb supported in a thermostatically controlled furnace, as used in our previous work (*Proc. Roy. Soc.*, 1953, A, 217, 563). The reaction was followed by means of a mercury manometer connected to the reaction vessel.

Results.—A typical plot of the logarithm of (initial pressure — pressure increase) against time is shown in Fig. 1. An initial fast reaction is observed, followed by a first-order reaction represented by the linear portion of the curve, which appears to accelerate after about two half-lives as is shown by the downward curvature of the plot. This curvature is believed to be caused by a secondary reaction of the products of the main reaction. The addition of toluene had no effect on the slope of the linear portion of the graph but eliminated the initial fast reaction. This was therefore supposed to be an alternative method of decomposition which proceeded by a free-radical chain mechanism; it was suppressed by the toluene when it was present or, when no toluene had been added, by the chain inhibitors (such as butene) produced in the decomposition. This hypothesis was tested by admitting more *tert.*-butylamine into the reaction vessel during a run. As predicted, the fast reaction did not recur.

The rate constant (k_3) for the secondary reaction (3) (the nature of which is discussed in a later section of this paper), was found by following the pressure increase after the main reaction had proceeded virtually to completion. It was assumed that this reaction also was a molecular split in which one of the product molecules split in two. Any other reasonable assumption would be equally good for the present purpose. Let k be the rate constant of the principal reaction; then $k \gg k_3$, and it can be shown that a correction for the second reaction may be

made by subtracting a quantity $p_0(1 - e^{-k_3 t})$ from the observed pressure at a time t , where p_0 is the initial pressure of the reactant. At 527° , k_3 was less than $0.05k$ and this simple correction was shown to be justified. k_3 was determined only at 527° because the measurement was lengthy and little error could be introduced by assuming that reaction (3) has the same temperature coefficient as the main reaction. An Arrhenius plot of the results is given in Fig. 2 for runs with initial pressures of reactant between 5 and 18 cm. The straight line corresponding to the equation $k = 6.1 \times 10^{14} \exp(-67,100/RT) \text{ sec.}^{-1}$ was obtained by the method of least squares, based only on the values obtained in an unpacked vessel in the absence of toluene. It can be seen that the values obtained in the presence of toluene and in a packed vessel of eight times the surface area of the unpacked vessel show no deviations outside the experimental error.

Analysis.—At the end of a run the stopcock S_1 was opened to admit the products into the analysis system shown in Fig. 3. At first with stopcocks S_2 and S_4 closed the gases were pumped by the two-stage mercury-diffusion pump P , through the pumped-down nitrogen-cooled trap

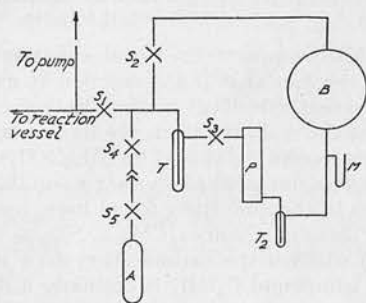


FIG. 3. Diagram of analysis apparatus.

T at -217° , into the 2-l. bulb B , to which a manometer M was attached. All the products except the hydrogen, which was subsequently identified by absorption in the heated copper oxide tube T_2 , were condensed out and the pressure of the hydrogen was measured.

T was then warmed to the temperature of liquid oxygen, and the pressure of methane measured, after which the non-condensable gases were pumped away. The pressures in the system when T was at a temperature of -78° and at room temperature were then measured. These measurements gave the pressure of products whose composition will be considered later, and the total amount of gas withdrawn from the reaction vessel. The whole mixture was then distilled into the bulb A , which contained an excess of previously degassed dilute sulphuric acid; A was removed from the system, allowed to warm, shaken to ensure satisfactory gas absorption, reattached to the vacuum-system, and cooled with solid carbon dioxide. Then the pressure of non-basic volatile gases was measured. As the amines present in the products were not volatile at -78° , the difference in the pressures read with the products at this temperature, before and after absorption, gave the pressure of ammonia in the products. The volatile products were then shaken with concentrated sulphuric acid to absorb unsaturated compounds. It was found that an amount of gas equal to the amount of hydrogen formed in the reaction was not absorbed by the acid. By its vapour pressure this gas was identified as propane. It was established empirically for seven runs that the identity

$$\text{Pressure of gas volatile at } -78^\circ = 2 \times \text{pressure of } \text{NH}_3 + 2 \times \text{pressure of } \text{H}_2$$

held. This was used for calculating the ratios of methane to ammonia produced. It may be interpreted by supposing that an amount of isobutene is formed equal to the amount of ammonia as is required by reaction (1), and that the hydrogen is produced by the secondary reaction (3) by which an equivalent amount of propane and of some other gas that is absorbed by sulphuric acid are also produced. We have not been able to continue a plausible reaction scheme to account for these products and they may be produced by a rather complex mechanism. However, the gases only represent some 4% of the total products. The hypothesis receives some confirmation from the reasonable agreement between the amount of hydrogen produced and the amount calculated by assuming that it is produced by reaction (3) (cf. cols. 5 and 6 of Table 2).

The complete analytical results, given in Table 2, show that the conversion calculated from the pressure change in the reaction vessel is always some 10–15% higher than that calculated from the analytical results except for the two runs to which toluene was added. We believe that the discrepancy is caused by the formation by the initial rapid reaction of products which

TABLE 2.

Run	Temp.	Total press.*	H ₂ *	H ₂ Total' %	Calc. % corr.	CH ₄ *	NH ₃ *	CH ₄ NH ₃	Conversion, %, by :	
									pressure change	analysis
16	498°	5.033	0.111	2.2	2.6	1.107	0.436	2.54	37.8	32.8
20	498	4.738	0.117	2.5	2.6	0.971	0.406	2.39	34.9	31.5
21	498	—	0.075	—	—	1.031	0.418	2.47	—	—
26A	516	4.868	0.091	1.9	1.2	0.845	0.330	2.56	29.6	26.0
29	516	4.715	0.110	2.3	1.8	0.965	0.378	2.55	35.0	—
30	516	5.120	0.116	2.3	1.7	0.984	0.374	2.63	34.9	28.8
33	541	—	0.108	—	—	0.911	0.348	2.62	—	—
35	541	—	0.084	—	—	0.781	0.336	2.32	—	—
37	541	—	0.103	—	—	0.948	0.385	2.46	—	—
† 48	§ 527	3.938	0.104	2.6	1.3	0.700	0.266	2.64	28.0	27.1
† 48A	§ 527	3.824	0.091	2.4	1.6	0.671	0.289	2.32	28.8	27.8
† 48B	§ 527	5.148	0.116	2.3	1.6	1.116	0.433	2.58	34.9	32.3
† 48C	527	5.061	0.127	2.5	1.5	1.047	0.366	2.86	34.1	30.5

* These pressures are in cm. in the analysis system and have no absolute significance.

† Run in packed vessel.

§ Run with added toluene.

polymerise on leaving the reaction vessel. This view is supported by the observation of a deposit in the connecting tubes and the trap *T*, and by the fact that if a correction is made for the products formed in the free-radical reaction the two methods of calculating the conversions agree very well. Accordingly, it may be concluded that the main reactions are those suggested here.

The exact nature of the substance C₃NH₇ is not known. It could be CMe₂.NH, which might well exist in the gas phase, or NH₂.CMe.CH₂. It does not seem likely that a suitable analytical method could be devised to detect these products in the quantities found here, but some light might be thrown on this problem by studying the decomposition of (CH₃)₃C.ND₂ as the methane formed would be CH₄ or CH₃D, depending upon whether the carbon atom drew its hydrogen from the amino- or from a methyl group. The compound C₃NH₇ is certainly a derivative of either the keto- or the enol form of acetone, for acetone diphenylhydrazone was obtained from the solution of the amine in dilute sulphuric acid.

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*The Reactions of Methyl Radicals with Acetone, Diethyl Ketone,
and Di-tert.-butyl Peroxide.*

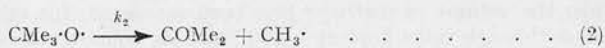
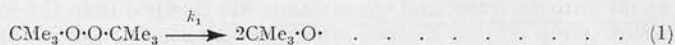
By G. O. PRITCHARD, H. O. PRITCHARD, and A. F. TROTMAN-DICKENSON.

[Reprint Order No. 4765.]

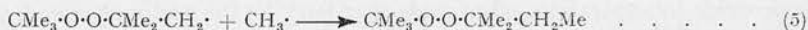
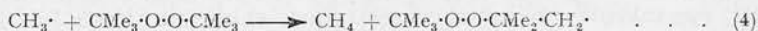
The thermal decomposition of di-*tert.*-butyl peroxide between 130° and 155° has been reinvestigated and the rate constant for the initial fission of the O-O bond found to be $4 \times 10^{16} e^{-39,000/RT}$ sec.⁻¹.

The rate constants for the hydrogen abstraction reactions of thermal methyl radicals with di-*tert.*-butyl peroxide, acetone, and diethyl ketone are given by $25 \times 10^{11} e^{-11,700/RT}$, $6.4 \times 10^{11} e^{-9500/RT}$, and $6.4 \times 10^{11} e^{-8000/RT}$ mole⁻¹ c.c. sec.⁻¹, respectively.

RALEY, RUST, and VAUGHAN (*J. Amer. Chem. Soc.*, 1948, **70**, 88) have shown that the thermal decomposition of di-*tert.*-butyl peroxide is an essentially non-chain unimolecular process, leading predominantly to the formation of acetone and ethane by the following mechanism:



A small amount of methane was formed, probably by the reactions



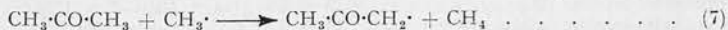
In the gas phase, in the presence of various organic substrates RH, the *tert.*-butoxy-radical is presumed to exhibit no other reactions than (2), which is very fast, but additional reactions of the type (6) can occur.



The purpose of this investigation was to use thermal methyl radicals to study reaction (6) for substances (RH) which are photolytic sources of higher radicals, and whose absorption spectra are such that they themselves would be photolysed if the usual photolytic sources of methyl radicals, dimethylmercury and acetone, were used.

Incidentally, the thermal decomposition of the peroxide was again studied, the rate being measured by the formation of ethane and methane, since the decomposition of each molecule of peroxide leads to the formation of either one molecule of ethane or one of methane.

If RH is acetone, (6) becomes



The acetylonyl radical then reacts with a methyl radical



to form ethyl methyl ketone. This compound was isolated by Raley, Rust, and Vaughan (*loc. cit.*) from the reaction products of the complete decomposition of the peroxide and was

presumably formed by the products of (2) reacting together according to (7) and (8). Consequently, to evaluate correctly the methane formed in (6), the methane formed from the products of (2) must be effectively suppressed. For this reason a high RH concentration is used, and only a small percentage of the peroxide is decomposed. The latter requirement is most important in the investigation of (4), because RH is now di-*tert*-butyl peroxide itself, and increase of its concentration only serves to increase the rate of (1) and thus the rate of (2) by a proportionate amount.

From the above reaction scheme the rate of methane formation is given by

$$d[\text{CH}_4]/dt = R_{\text{CH}_4} = k_6[\text{CH}_3\cdot][\text{RH}]$$

and of ethane by

$$d[\text{C}_2\text{H}_6]/dt = R_{\text{C}_2\text{H}_6} = k_3[\text{CH}_3\cdot]^2$$

whence

$$k_6/k_3^{1/2} = R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}[\text{RH}]$$

The plot of $\log k_6/k_3^{1/2}$ against $1/T$ gives $E_6 - \frac{1}{2}E_3$ and $A_6/A_3^{1/2}$, where T is the absolute temperature, E is the activation energy, and A is the frequency factor. By using Gomer and Kistiakowsky's values (*J. Chem. Physics*, 1951, **19**, 85) of $E_3 = 0$ kcal./mole and $A_3 = 4.5 \times 10^{13}$ mole⁻¹ c.c. sec.⁻¹ for the recombination of methyl radicals, E_6 and A_6 can be obtained.

Experimental.—The method was to mix measured pressures of the peroxide and ketone in a 2-l. volume surrounded by a steam jacket. This mixture was expanded into a 3-l. reaction vessel immersed in an oil-bath thermostat which could be controlled to $\pm 0.1^\circ$ for the period of an experiment. The reaction was terminated by pumping the reactants and products through wide-bore tubing and a liquid-nitrogen trap into a 3-l. bulb. The ethane was collected in liquid-nitrogen traps, and the methane was pumped from the collecting system by a mercury diffusion pump into an analysis system, which consisted of a Töpler pump and a gas burette. When the volume of methane had been measured, the ethane was pumped into the analysis system through traps kept at -160° , and its volume measured.

RESULTS AND DISCUSSION

In all the runs about 10% of the peroxide was decomposed. When RH was ketone, [RH] was taken as the initial concentration, which was always 1.5–3 times greater than the peroxide concentration. Not more than 0.5% of the acetone reacted, yielding 7–14% of methane of the total methane and ethane formed, and between 2 and 4% of the diethyl ketone reacted, the amount of methane formed varying between 31 and 55%.

When RH was di-*tert*-butyl peroxide, [RH] was taken as the arithmetic mean of the initial and final concentrations of the peroxide, the proportion of methane formed being between 2 and 3%.

The values of E_1 , A_1 , and k_1 at 145° which have been obtained from Fig. 1 are given in Table 1, together with experimental values of other workers. The present results are seen to lead to a value of E_1 of 39 ± 0.5 kcal./mole, with A_1 about 4×10^{16} sec.⁻¹.

TABLE 1.

System *	E_1 , kcal./mole	A_1 , sec. ⁻¹	k_1 , sec. ⁻¹ (145°)	Source †
Peroxide	38.6	1.9×10^{16}	1.3×10^{-4}	This work
Peroxide-acetone	39.5	5.9×10^{16}	1.3×10^{-4}	"
Peroxide-diethyl ketone	39.5	6.8×10^{16}	1.5×10^{-4}	"
Peroxide	39.1	3.2×10^{16}	1.1×10^{-4}	a
Peroxide	36–40	6×10^{14} – 6×10^{16}	1×10^{-4}	b
Peroxide-acetone	37	9×10^{14}	0.6×10^{-4}	c
Peroxide-toluene (flow system) ...	36 ± 1	4×10^{14} – 7×10^{14}	1.3×10^{-4}	d
Peroxide-toluene (static system) ...	34 ± 2	4×10^{13}	0.6×10^{-4}	d
Peroxide	38	7×10^{15}	—	e

* Peroxide = di-*tert*-butyl peroxide.

† a, Raley, Rust, and Vaughan, *loc. cit.*; b, Brinton and Volman, *J. Chem. Physics*, 1952, **20**, 25; c, Jaquiss, Roberts, and Szwarc, *J. Amer. Chem. Soc.*, 1952, **74**, 6005; d, Murawski, Roberts, and Szwarc, *J. Chem. Physics*, 1951, **19**, 698; e, Lossing and Tickner, *J. Chem. Physics*, 1952, **20**, 907 [this is a composite result of the high-temperature runs (280 – 350°) of these authors together with the results of a and d].

In Table 2 the values of E_6 , A_6 , and k_6 at 182° obtained from Fig. 2 are given, together with the results of other workers.

The activation energy obtained for the reaction of methyl radicals with acetone is in excellent agreement with the results of other workers, using both photolytic and thermal methyl radicals. There is a sensible decrease in the activation energy obtained for the reaction with diethyl ketone, in accordance with the general trend exhibited by compounds containing only primary hydrogen atoms, and those containing both primary and secondary hydrogen atoms.

TABLE 2.

RH *	E_6 , kcal./mole †	A_6 , mole ⁻¹ c.c. sec. ⁻¹	k_6 , mole ⁻¹ c.c. sec. ⁻¹ (182°)	Source ‡
Acetone	9.5 ± 0.3	6.4 × 10 ¹¹	1.6 × 10 ⁷	This work
"	9.7 ± 0.1	4.0 × 10 ¹¹	1.0 × 10 ⁷	a
"	9.6 ± 0.4	3.0 × 10 ¹¹	0.8 × 10 ⁷	b §
"	9.5 ± 0.2	4.0 × 10 ¹¹	1.1 × 10 ⁷	c
"	9.5 ± 1.0	2.7 × 10 ¹¹	0.9 × 10 ⁷	d
Diethyl ketone	8.0 ± 0.2	6.4 × 10 ¹¹	9.1 × 10 ⁷	This work
Peroxide	11.7 ± 0.3	25 × 10 ¹¹	0.6 × 10 ⁷	"
Peroxide	(15)	(300 × 10 ¹¹)	0.2 × 10 ⁷	e §

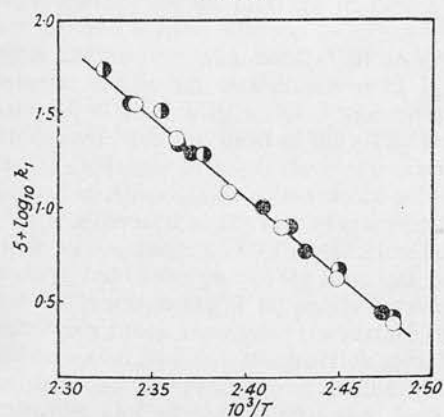
* Peroxide = di-*tert.*-butyl peroxide.

† The probable errors in the activation energies are derived solely from consideration of the deviations of the points from the Arrhenius relationship.

‡ a, Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1950, **18**, 1097; b, Saunders and H. A. Taylor, *ibid.*, 1941, **9**, 616; c, Gomer and Kistiakowsky, *loc. cit.*; d, Jaquiss, Roberts, and Szwarc, *loc. cit.*; e, Brinton and Volman, *loc. cit.*

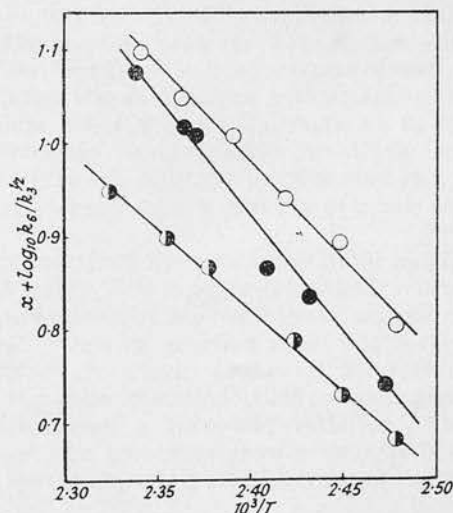
§ These quantities were not calculated in this manner by the original authors (see Trotman-Dickenson, *Quart. Reviews*, 1953, **7**, 198).

FIG. 1.



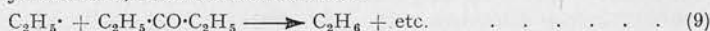
Arrhenius plots for the thermal decomposition of di-*tert.*-butyl peroxide: ● alone, ○ in the presence of acetone, and ◐ in the presence of diethyl ketone.

FIG. 2.



Arrhenius plots for reaction of methyl radicals with: ○ Acetone, $x = 1$, ◐ diethyl ketone, $x = 0$, and ● di-*tert.*-butyl peroxide, $x = 1.48$.

Kutschke, Wijnen, and Steacie (*J. Amer. Chem. Soc.*, 1952, **74**, 714), using diethyl ketone as a source of ethyl radicals, studied the reaction



They found $E_9 = 7.4$ kcal./mole, with a steric factor of about 3×10^{-4} . The greater energy of activation required for the methyl (8.0 kcal./mole) than the ethyl (7.4 kcal./mole) radical reaction is surprising, for one would expect that the ethyl radical reaction would require, if anything, a slightly higher activation energy than the methyl radical reaction, because the C-H bond strength in methane exceeds that in ethane by about 5 kcal./mole.

The activation energy for methyl radical attack on di-*tert.*-butyl peroxide is surprisingly

high, only methane requiring a higher activation energy of approximately 12.8 kcal./mole (Trotman-Dickenson and Steacie, *J. Phys. Colloid Chem.*, 1951, **55**, 908), whilst other compounds containing only primary C-H bonds have lower activation energies than the 11.7 kcal./mole required for di-*tert.*-butyl peroxide; *e.g.*, ethane 10.4 and 2:2:3:3-tetramethylbutane 9.5 kcal./mole (Trotman-Dickenson, Birchard, and Steacie, *J. Chem. Physics*, 1951, **19**, 163). The reason why this should be is not clear.

One of us (G. O. P.) wishes to thank the Department of Scientific and Industrial Research for a maintenance grant.

UNIVERSITY OF MANCHESTER.

[Received, November 3rd, 1953.]

The Exchange of Iodine Atoms between Iodine and Methyl Iodide in the Temperature Range 150—375°.

By DOUGLAS CLARK, H. O. PRITCHARD, and A. F. TROTMAN-DICKENSON.

[Reprint Order No. 4863.]

OGG and POLANYI (*Trans. Faraday Soc.*, 1935, **31**, 482) showed that the reaction between iodine atoms and *sec.*-butyl iodide leads to optical inversion of the butyl iodide molecule. They found that below 200° the racemisation was a heterogeneous reaction of low activation energy (8 kcal./mole), but that in the temperature range 240—280° the homogeneous inversion by iodine atoms predominated because of its considerably higher activation energy (32.2 kcal./mole); the investigation was complicated, however, by the fact that at these temperatures the butyl iodide molecule is unstable. In an attempt to gain a better understanding of the factors affecting these inversion reactions, we have studied the exchange of ¹³¹I atoms between iodine and methyl iodide vapours, hoping to follow the very simplest example of an inversion reaction, *i.e.*,

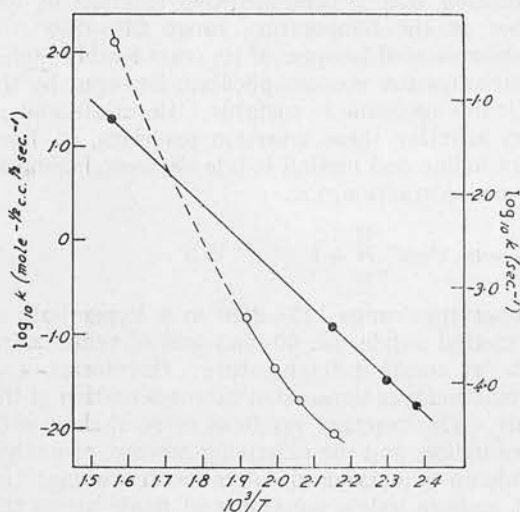


The reaction was studied over the temperature range 185—250° in a Pyrex bulb of about 1 l. capacity: known pressures of methyl iodide (*ca.* 50 cm.) and of radio-iodine (*ca.* 1 cm.) were introduced into the bulb (at constant temperature; thermostat) and allowed to react; after a known time, the reaction was terminated by condensation of the iodine-methyl iodide mixture in liquid air. The reaction products were shaken with mercury and a little acetone to remove free iodine, and the remaining mixture of methyl iodide and acetone was distilled off and made up to a standard volume with acetone; the mercuric iodide left was dissolved in 10% sodium iodide solution and made up to the standard volume with water. The extent to which the reaction had occurred was then determined from the ratio of the γ -ray activities of the two solutions (tests showed only a minute difference between the γ -ray assay obtained when a known quantity of iodine was counted in either aqueous or acetone solution).

It was found that the rate of transference of radioactivity from the iodine to the methyl iodide was represented by the equation $\text{Rate} = k[\text{MeI}][\text{I}_2]^{\frac{1}{2}}$, as is required for the inversion reaction, but that a plot of $\log k$ against $1/T$ was not a straight line (see Figure), suggesting that the reaction might be partly heterogeneous. When the reaction vessel was packed with Pyrex tubes, increasing the surface to volume ratio by a factor of about 8, the reaction rate increased 30-fold; the reaction remained of first order in methyl iodide concentration, but became independent of iodine concentration over a three-fold variation. The Arrhenius plot of these first-order, heterogeneous rate constants gives a straight line, roughly parallel to the lower portion of the plot for the unpacked vessel, corresponding to an activation energy of about 17 kcal./mole.

By analogy with Ogg and Polanyi's results, we assumed that the reaction occurred by two mechanisms, one heterogeneous having an activation energy of about 17 kcal./mole, the other homogeneous having a higher activation energy; if this were the case, higher temperatures would favour the latter reaction, and in order to try to isolate this reaction, experiments were carried out at 375° in a conventional flow pyrolysis apparatus (Leigh, Sehon, and Szwarc, *Proc. Roy. Soc.*, 1951, **A**, 209, 97). The reactants were introduced into the reaction zone, methyl iodide vapour at about 8 mm. pressure being used as a carrier for the iodine; the rate of flow of methyl iodide was adjusted to give a contact time of about $\frac{3}{4}$ sec., and the iodine pressure was adjusted to give about the same ratio of $[\text{MeI}]/[\text{I}_2]$ as in the static experiments. A point representing the mean of several bimolecular rate constants is shown in the Figure as a continuation of the Arrhenius curve, since the surface to volume ratios for the two unpacked reaction vessels were not very different. However, packing the reaction vessel showed that even at this temperature the

reaction was largely heterogeneous, and the heterogeneous rate was still dependent only on the methyl iodide concentration. Two types of packing were used in testing for heterogeneity in the flow system. In one set of experiments the reaction zone was packed completely with short lengths of Pyrex tube, resulting in a 6-fold increase in surface to volume ratio; the rate of the reaction increased by a factor of 6 as a result. The rate constants obtained were scaled up in the ratio of 8 to 6 to allow for the disparity in surface to volume ratios of the two packed reaction vessels, and the mean point thus obtained was found to lie very close to the continuation of the Arrhenius plot for the heterogeneous reaction observed at lower temperatures; the best line through all these points represents an activation energy of 17.0 kcal./mole.



Arrhenius plots for the exchange of radio-iodine with methyl iodide:

○ in an unpacked reaction vessel,
● in a packed reaction vessel.

A second type of packing, which has sometimes been used in kinetic studies, was also tried: enough quartz fibre to increase the surface area of the effective reaction zone by a factor of 4–5 was introduced into the vessel; the volume of this packing was quite small and it lay on the floor of the reaction vessel, occupying only about one-fifth of the volume of the reaction zone. No increase in reaction rate was observed under these conditions, suggesting that with contact times as short as those used here, the main body of the gas streams through the reaction vessel without coming into contact with the fibre packing. Such observations must cast some doubt on the interpretation of those kinetic measurements in which this type of packing was used, as it seems only to provide a stringent test for heterogeneity when it is distributed throughout the whole cross-section of the reaction zone.

These experiments show that it is not possible to isolate the reaction of higher activation energy, which probably represents the inversion of methyl iodide by iodine atoms (because of the nature of the kinetics in the unpacked vessels) at temperatures at which methyl iodide is stable; the only conclusion we can draw is that, from the slope of the upper portion of the Arrhenius curve, the activation energy is certainly not less than the 32.2 kcal./mole observed by Ogg and Polanyi for *sec.*-butyl iodide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER]

The Study of Chlorine Atom Reactions in the Gas Phase

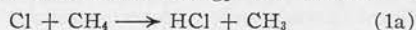
By H. O. PRITCHARD, J. B. PYKE^{1a} AND A. F. TROTMAN-DICKENSON^{1b}

RECEIVED NOVEMBER 19, 1954

The rates of chlorine atom attack on the following compounds: methane, ethane, propane, 2-methylpropane, 2,2-dimethylpropane, cyclopentane, methyl chloride and ethyl chloride, have been related to the rate of the reaction $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$. The rate factors listed in Table II were deduced from measurements made in the temperature range from 0 to 300°. The activation energies are lowest for those compounds which contain the weakest C-H bonds, but the activation energies and bond strengths are not linearly related. The most reactive compounds react with activation energies less than 1 kcal. No evidence is found for A (pre-exponential) factors greater than the collision rates.

The reactions of chlorine atoms with hydrogen-containing compounds are chain reactions, and as such their over-all rates are very sensitive to the presence of small traces of impurity, to the condition of the surface of the reaction vessel and, in photochemical systems, to the intensity of the absorbed light. Consequently the many attempts which have been made to determine rate constants for the elementary reactions of chlorine atoms have met with disproportionately little success. However, Tamura² was able to set an upper limit of 6

kcal. for the activation energy of reaction 1a.



Schumacher and Wolff³ obtained $E < 4.3$ kcal. for the similar reaction with chloroform.

The rate constant of reaction 1b is known accurately over the temperature range 273 to 1050°K.



from the work of Ashmore and Chanmugam,^{4a} Steiner and Rideal^{4b} and Rodebush and Klingel-

(1) (a) College of Forestry, N. Y. State University, Syracuse 10, N. Y.; (b) Chemistry Department, The University, West Mains Road, Edinburgh 9.

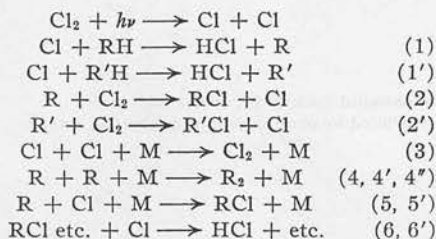
(2) M. Tamura, *Rev. Phys. Chem. Japan*, **15**, 86 (1941).

(3) H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, **B25**, 161 (1934).

(4) (a) P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953); (b) H. Steiner and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A173**, 503 (1939).

hoeffer.⁵ When methane reacts with chlorine in the presence of hydrogen, it is possible to determine accurately the rate of the reaction 1a without any direct knowledge of the chlorine atom concentration, solely by measurement of the relative proportions of hydrogen and methane used up. Similarly the rate of reaction of methane can be compared with that of another hydrocarbon RH. Thus a whole series of reaction rates, based on the assumed value for the rate constant of reaction 1b, may be established.

When a mixture of two hydrocarbons and chlorine is illuminated, the following reactions are possible



RH and R'H are only removed by reactions 1 and 1'. Now it can be readily shown⁶ that if

$$-\frac{d[\text{RH}]}{dt} = k_1[\text{RH}][\text{Cl}] \quad \text{and} \quad -\frac{d[\text{R}'\text{H}]}{dt} = k_1'[\text{R}'\text{H}][\text{Cl}]$$

then

$$\frac{k_1}{k_1'} = \log \frac{[\text{RH}]_i}{[\text{RH}]_f} \bigg/ \log \frac{[\text{R}'\text{H}]_i}{[\text{R}'\text{H}]_f} \quad (I)$$

where the subscripts *i* and *f* refer to the initial and final concentrations of the reactants. Equation I will only break down if there is a significant back reaction -1 or -1'; evidence on this point will be presented later.

We originally hoped to establish a complete series of reactivities starting from hydrogen and working upwards, but there was a large difference in the reactivities of methane and ethane. A number of likely substances were tried which we thought might be of intermediate reactivity, but it was found impossible to bridge the gap indirectly. We were forced to compete methane and ethane directly; this comparison is therefore rather less accurate than the others.

Experimental

Approximately 2.5×10^{-4} mole of chlorine was measured out and distilled into a 160-ml. Pyrex reaction vessel cooled in liquid nitrogen. Known quantities of the two competing gases were then admitted and the vessel was sealed off from the vacuum system. The reaction vessel was placed in one of a number of constant temperature baths and allowed to warm up to bath temperature in complete darkness. It was then strongly illuminated for about an hour with light from a tungsten filament lamp to ensure complete reaction of the chlorine. Finally the reaction vessel was reattached to the vacuum system, the seal broken and the contents analyzed by fractional distillation as follows (the optimum conditions being determined by trial on known mixtures).

Methane-Hydrogen Mixtures.—The contents of the vessel were hydrogen chloride, methyl chloride (and some polychlorinated methanes) together with the residual methane and hydrogen. The further chlorination of the methyl chloride does not invalidate equation I, but means that the

amounts of HCl and CH_3Cl produced cannot be used as a check on the results. The methane and hydrogen were separated easily from the other compounds because they are volatile at the boiling point of liquid nitrogen. They were pumped through a trap containing silica gel⁷ at -193° ; this removed the methane quantitatively, and upon warming up to room temperature released it completely. The volumes of residual hydrogen and methane were then measured separately. Runs were carried out at 20, 60, 100, 135, 146, 168, 211° ; for range of concentrations used, see Table I.

TABLE I

Methane + hydrogen at 100° ; amount of Cl_2 added = $15.5 (\pm 1.0) \times 10^{-7}$ mole/cc.

Initial concn., moles/cc.	Initial concn., moles/cc.	Amount reacted, moles/cc.	Amount reacted, moles/cc.	k_1/k_1'
$10^7[\text{H}_2]$	$10^7[\text{CH}_4]$	$10^7\Delta[\text{H}_2]$	$10^7\Delta[\text{CH}_4]$	
28.34	27.96	2.22	6.96	2.76
35.98	44.81	2.75	8.98	2.81
58.15	52.19	4.72	7.54	3.01
66.57	33.80	5.27	6.46	2.57
76.77	33.27	5.24	7.72	2.88
81.34	51.16	4.09	8.62	2.79

Methane-Methyl Chloride Mixtures.—The residual methane was removed by pumping at liquid nitrogen temperature. The rest of the contents were then distilled on to solid KOH to remove the HCl leaving methyl chloride and substituted methyl chlorides, the former being collected by controlled distillation at -125° . Runs were carried out at 25, 76, 100, 146, 211° ; range of concentrations used; $[\text{CH}_4] = 30-90 \times 10^{-7}$, $[\text{CH}_3\text{Cl}] = 25-72 \times 10^{-7}$ mole/cc.

Methane-Ethane Mixtures.—The procedure was as for methane-methyl chloride mixtures except that ethane for analysis was pumped off at -165° . Runs were carried out at 76, 100, 146, 211° ; range of concentrations used: $[\text{CH}_4] = 65-81 \times 10^{-7}$, $[\text{C}_2\text{H}_6] = 14-20 \times 10^{-7}$ mole/cc.

Ethane-Ethyl Chloride Mixtures.—After the HCl had been removed the ethane was pumped off at -165° and the ethyl chloride at -102° . Runs were carried out at 25, 100, 146, 211° ; range of concentrations used: $[\text{C}_2\text{H}_6] = 34-64 \times 10^{-7}$, $[\text{C}_2\text{H}_5\text{Cl}] = 43-95 \times 10^{-7}$ mole/cc.

Ethane-Propane Mixtures.—The propane was removed at -133° . Runs were carried out at 25, 100, 146, 211° ; range of concentrations used: $[\text{C}_2\text{H}_6] = 18-36 \times 10^{-7}$, $[\text{C}_3\text{H}_8] = 19-66 \times 10^{-7}$ mole/cc.

Ethane-Butane and Ethane-Pentane Mixtures.—Because the heavier hydrocarbons and ethyl chloride have similar boiling points, they were collected together and measured. The amount of the heavier hydrocarbon was then found by subtraction of the amount of ethyl chloride present, which was calculable from the amount of ethane used up. Runs with these mixtures were carried out at 25, 76, 146, 211° ; range of concentrations used: $[\text{C}_2\text{H}_6] = 20-60 \times 10^{-7}$, $[\text{C}_4\text{H}_{10}] = 20-28 \times 10^{-7}$, $[\text{C}_5\text{H}_{12}] = 18-29 \times 10^{-7}$, $[\text{C}_6\text{H}_{14}] = 33-65 \times 10^{-7}$ mole/cc.

Very considerable care was taken in all cases that the components of the reacting mixtures were of the highest possible purity.

Results

The calculation of results according to equation I was quite straightforward except when methane-methyl chloride and ethane-ethyl chloride mixtures were being investigated. Then one of the products of chlorination was the other member of the mixture. Consequently equation I had to be modified. Some three to six runs were performed at each temperature. A specimen set of results for methane and hydrogen are given in Table I. The complete activation energy difference plot is shown in Fig. 1.

When $\text{R}'\text{H} \equiv \text{RCI}$ a more complicated form of expression is needed, viz.

$$\frac{k_1}{k_1'} = \frac{\log(A_i/A_f)}{\log \frac{B_i - k_1 A_i / (k_1' - k_1)}{B_f - k_1 A_f / (k_1' - k_1)}} \quad (II)$$

(5) W. H. Rodebush and W. K. Klingelhoeffer, *THIS JOURNAL*, **55**, 130 (1933).

(6) W. M. Jones, *J. Chem. Phys.*, **19**, 78 (1951).

(7) R. Delaplace, *Compt. rend.*, **205**, 664 (1937).

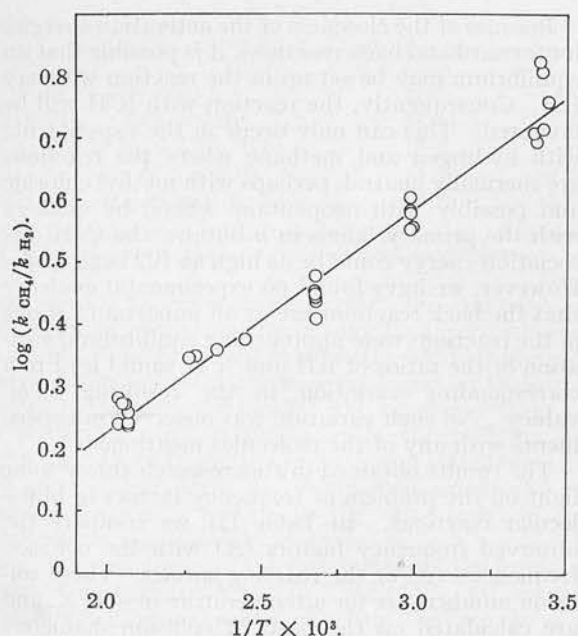


Fig. 1.—The relative rates of chlorination of hydrogen-methane mixtures.

where A is $[RH]$ and B is $[RCl]$. The expression cannot be simplified to obtain k_1/k_1' explicitly. Furthermore, in our experiments, it was found that the optimum experimental conditions for ease of analysis led to a situation where A/B was of the same order of magnitude as $(k_1' - k_1)/k_1$, so that expression II became extremely sensitive to small experimental errors. This difficulty was overcome by considering the two limiting cases (a) that the RCl produced from RH does not react, and (b) that all the RCl produced from RH is available for reaction from the commencement of the run, leading to

$$\frac{k_1}{k_1'} = \frac{\log(A_i/A_f)}{\log \frac{B_i}{B_f - (A_i - A_f)}} \quad (\text{IIa})$$

and

$$\frac{k_1}{k_1'} = \frac{\log(A_i/A_f)}{\log \frac{B_i + (A_i - A_f)}{B_f}} \quad (\text{IIb})$$

In practice these two estimates of the rate ratios did not differ by more than 12% when R was CH_3 and they were often much closer than this. When R was C_2H_5 , the differences were of the order of 10–20%. In each case, the average result from (IIa) and (IIb) was used to calculate activation energy differences.

When $B_i = 0$, equation II becomes

$$B_f = \frac{k_1 A_f}{k_1' - k_1} \left\{ 1 - \left(\frac{A_i}{A_f} \right)^{(k_1 - k_1')/k_1} \right\} \quad (\text{IIc})$$

Sometimes the ethyl chloride produced was not separable from the residual gases, as when the ethane-pentane systems were studied. Then the amount of ethyl chloride was estimated from equation IIc, using the values of k_1 and k_1' which had previously been determined.

The mixtures investigated and the experimental temperature coefficients are listed in Table II and

TABLE II

Mixture RH + R'H	A_1'/A_1	$E_1 - E_1'$, cal./mole	$\frac{A_1'}{A_1} \times 10^{-14}$, moles ⁻¹ cc. sec. ⁻¹	E_1' , cal./mole
H ₂ + CH ₄	0.32	1650 ± 150	0.26	3850
CH ₄ + CH ₃ Cl	2.22	490 ± 150	0.57	3360
CH ₄ + C ₂ H ₆	4.67	2850 ± 370	1.20	1000
C ₂ H ₆ + C ₂ H ₅ Cl	0.38	-490 ± 90	0.46	1490
C ₂ H ₆ + CH ₂ (CH ₃) ₂	1.47	330 ± 200	1.76	670
C ₂ H ₆ + CH(CH ₃) ₂	1.64	140 ± 20	1.96	860
C ₂ H ₆ + C(CH ₃) ₄	1.03	300 ± 40	1.23	700
C ₂ H ₆ + cyclo-C ₄ H ₁₀	2.45	420 ± 40	2.93	580

the experimental points are plotted in Fig. 2. The experimental uncertainties are represented by an error quoted on the activation energy differences; these errors were estimated from the scatter of the Arrhenius plots. The values in the columns headed A_1' and E_1' are calculated from columns two and three of the table together with the rate expression for hydrogen itself, viz., $k_{1b} = 0.79 \times 10^{14}$ exp. $(-5500 \pm 200/RT)$ mole⁻¹ cc. sec.⁻¹.

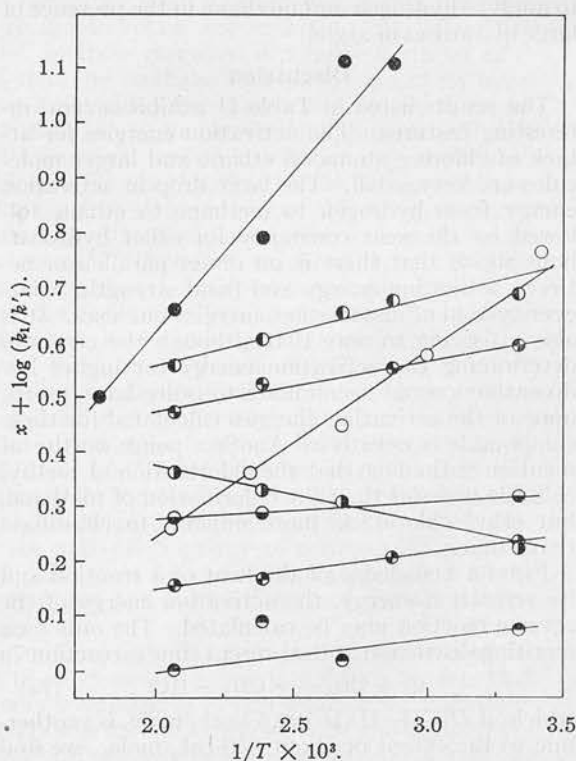


Fig. 2.—The relative rates of chlorination of mixtures: O, hydrogen + methane ($x = 0$); ●, methane + methyl chloride ($x = 0$); ●, methane + ethane ($x = -1.3$); ●, ethane + ethyl chloride ($x = 1.0$); ●, ethane + propane ($x = -0.3$); ●, ethane + isobutane ($x = 0$); ●, ethane + neopentane ($x = 0$); ●, ethane + cyclopentane ($x = -0.1$). (Each point represents the mean of all experiments carried out at that temperature; the relative rate equations were calculated from the data for the individual experiments by the method of least squares.)

Returning to the problem of bridging the gap in reactivity between methane and ethane, it might be thought from the results in Table II that methyl chloride would provide the answer. But the values

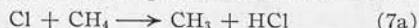
of $k_{\text{MeCl}}/k_{\text{EtH}}$ apparently showed a maximum at 100° and fell away at both higher and lower temperatures. Probably this strange result was obtained because it was impossible to separate ethyl chloride, methyl chloride and methylene dichloride by distillation, so that the extent of the reaction had to be estimated indirectly. Experiments were also carried out with ethane and chloroform, ethane and dimethyl ether and with ethane and benzene mixtures. Dimethyl ether chlorinates approximately twice as fast as ethane both at 25 and 146°; benzene and chloroform appeared to react at about the same rate as ethane, but more moles of ethane were used up than the number of moles of chlorine originally added. We have not sufficient analytical evidence to account satisfactorily for this.

The possibility that "hot" chlorine atoms may be involved was investigated by adding about 20 cm. of argon to some of the ethane-isobutane mixtures. No difference in rate ratios was observed. The addition of an inert gas to hydrogen-methane mixtures would have been a more rigorous test, but it is difficult to analyze hydrogen and methane in the presence of large quantities of argon.

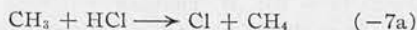
Discussion

The results listed in Table II exhibit several interesting features. The activation energies for attack of chlorine atoms on ethane and larger molecules are very small. The large drop in activation energy from hydrogen to methane to ethane followed by the near constancy for other hydrocarbons shows that there is no direct parallelism between activation energy and bond strength, whatever system of dissociation energies one uses. It is also satisfying to note that although the errors in determining the activation energy for higher hydrocarbons could accumulate to quite large totals, none of the activation energies calculated for these compounds is negative. Another point worthy of mention is the fact that the chlorination of methyl chloride is easier than the chlorination of methane, but ethyl chloride is more difficult to chlorinate than ethane.

From a knowledge of the heat of a reaction and its activation energy, the activation energy of the reverse reaction may be calculated. The only case meriting discussion at the present time is reaction 7a



which, if $D(\text{CH}_3\text{-H})$ is 102.5 kcal./mole, is exothermic to the extent of about 650 cal./mole; we find that the activation energy of the reaction is 3850 cal./mole, so that the activation energy of reaction -7a



must be 4.5 kcal. The reaction of methyl radicals with hydrogen chloride has been studied recently by Cvetanović and Steacie⁸ who concluded that the activation energy was about 2.1 kcal./mole, but their results were not very reproducible. From their experiments at 28° they quote an upper limit of 5.1 kcal. which is consistent with our observations.⁹

Because of the closeness of the activation energies for forward and back reactions, it is possible that an equilibrium may be set up in the reaction with say RH. Consequently, the reaction with R'H will be favoured. This can only occur in the experiments with hydrogen and methane where the reactions are thermally neutral, perhaps with methyl chloride and possibly with neopentane where, by analogy with the primary bonds in *n*-butane, the C-H dissociation energy could be as high as 102 kcal./mole. However, we have found no experimental evidence that the back reactions are at all important; if one of the reactions were approaching equilibrium, variation of the ratios of RH and R'H would lead to a corresponding variation in the resulting k_1/k_1' values. No such variation was observed in experiments with any of the molecules mentioned.

The results obtained in this research throw some light on the problem of frequency factors in bimolecular reactions. In Table III we compare the observed frequency factors (A) with the collision frequencies (Z) of the reacting species. These collision numbers are for a temperature of 400°K. and are calculated on the basis of collision diameters taken from a recent paper by Rowlinson¹¹; the collision diameter for chlorine has been taken to be the same as that for argon (3.42 Å.). In the final column of Table III, the quantities A/Z are listed and we will loosely identify these ratios with the steric factors for the reactions; to attach any precise significance to the ratio A/Z involves a knowledge of the number of square terms contributing to the reaction. The quantity A/Z is never significantly greater than unity and we may therefore conclude that the chlorine atom reactions studied here do not have steric factors greater than unity. However, steric factors considerably greater than unity have been reported for the corresponding reactions of bromine atoms.¹² It is interesting that bromine should react with 2-methylpropane or 2,2-dimethylpropane with frequency factors of the order of 10^{17} mole⁻¹ cc. sec.⁻¹ whereas chlorine reacts with the same substances with "normal" frequency factors. This large difference cannot be

TABLE III

Reactant	Collision diameter, Å.	$10^{-14}Z$, moles ⁻¹ cc. sec. ⁻¹	$10^{-14}A$	A/Z
H ₂	2.93	4.04	0.79	0.20
CH ₄	3.85	2.20	.26	.12
CH ₃ Cl	4.1 ^a	1.69	.57	.3
C ₂ H ₆	4.30	2.04	1.20	.6
C ₂ H ₅ Cl	4.5 ^a	1.79	0.46	.3
C ₃ H ₈	4.75	2.07	1.76	.9
Iso-C ₄ H ₁₀	5.20	2.18	1.96	.9
Neo-C ₄ H ₁₂	5.45	2.23	1.23	.6
Cyclo-C ₅ H ₁₀	5.4 ^a	2.21	2.93	1.3

^a Estimated.

errors. k_{7a} was given as $10^{14.5}$ exp. $(-3800/RT)$ mole⁻¹ cc. sec.⁻¹, whereas $10^{13.4}$ exp. $(-3850/RT)$ is correct. Consequently, k_{-7a} should have been $10^{12.1}$ exp. $(-4510/RT)$ which is equal to $10^{9.8}$ at 150°. The agreement with the value of $10^{10.4}$ given by Cvetanović and Steacie is as good as was reported previously.

(10) H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *This Journal*, **76**, 1201 (1954).

(11) J. S. Rowlinson, *Quart. Rev.*, **8**, 168 (1954).

(12) B. H. Eckstein, H. A. Scheraga and E. R. Van Artsdalen, *J. Chem. Phys.*, **22**, 29 (1954).

(8) R. J. Cvetanović and E. W. R. Steacie, *Can. J. Chem.*, **31**, 518 (1953).

(9) A preliminary note¹⁰ on this topic contained some arithmetical

TABLE IV
 A 's in mole⁻¹ cc. sec.⁻¹, E 's in kcal./mole.

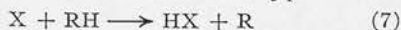
Reaction	log A expt.	E	Ref.	log A calc.	Ref.
Cl + CH ₄ → HCl + CH ₃ (7a)	13.4	3.9	This work	13.0	This work ^a
H + CH ₄ → H ₂ + CH ₃ (7b)	12.5	9.0	See discussion	13.3	16
CH ₃ + CH ₄ → CH ₄ + CH ₃ (7c)	11.5	14.3	14	10.9	16
Br + CH ₄ → HBr + CH ₃ (7d)	13.7	18.3	15	13.7	15

^a The transition state calculation was made by standard methods.¹⁶ The H-Cl distance was assumed to be 1.65 Å. and the C-H-Cl doubly degenerate bending frequency was taken as 500 cm.⁻¹.

accounted for by experimental errors, but the possibility still remains that there may be an error in the assumed reaction mechanisms (the bromination of neopentane experiments were criticised on these grounds by Benson and Graff¹³ who suggested that the neopentyl radicals produced in the reaction might decompose to methyl radicals and isobutene; they showed that such an assumption would reduce the frequency factors to the same order of magnitude as the collision number).

We may now consider the rate factors of the four reactions of methane listed in Table IV. All are taken directly from the sources except the rate factors of reaction 7b. We have estimated these as follows: The activation energy of reaction -7b is 10.0 kcal./mole,¹⁷ and reaction 7b is approximately 1 kcal./mole exothermic. Therefore the activation energy of reaction 7b is 9 kcal./mole. The A factor of reaction -7b is 10^{11.5} mole⁻¹ cc. sec.⁻¹. From considerations of the entropies of the substances involved in the reaction¹⁸ we can show that $A_{7b}/A_{-7b} \approx 10$. Therefore A_{7b} is 10^{12.5} mole⁻¹ cc. sec.⁻¹; if anything this value is likely to be a little high. These rate factors give $k_{7b} = 10^{7.7}$ mole⁻¹ cc. sec.⁻¹ at 140°, which value agrees far better than could be reasonably hoped with the value of 10^{7.6} mole⁻¹ cc. sec.⁻¹ measured by Berlie and LeRoy.¹⁹ They found that $k_{7b} = 10^{10.0} \exp.(-4500/RT)$ mole⁻¹ cc. sec.⁻¹, but placed much more reliance on their measurement of the reaction rate than of its temperature dependence. Indeed, measurements of rates are generally much more reliable than measurements of temperature coefficients. It can be seen from the table that all of these A factors are in reasonable agreement with the predictions of transition state theory listed in the fifth column.

It is often suggested, as a rough corollary of the supposed activation energy-dissociation energy relationship, that in a reaction of the type



the stronger the HX bond, the lower the activation energy and it is instructive to examine this hypothesis.

(13) S. W. Benson and H. Graff, *J. Chem. Phys.*, **20**, 1182 (1952).

(14) J. R. McNesby and A. S. Gordon, *THIS JOURNAL*, **76**, 4196 (1954).

(15) G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

(16) S. Bywater and R. Roberts, *Can. J. Chem.*, **30**, 773 (1952).

(17) E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953).

(18) A. F. Trotman-Dickenson, *ibid.*, **21**, 211 (1953).

(19) M. R. Berlie and D. J. LeRoy, *Can. J. Chem.*, **32**, 650 (1954).

sis in the light of data now available. Consider the activation energies of the three reactions 7a, 7b and 7c. The bonds formed in the three reactions have identical dissociation energies to within about $\pm 1\%$; hence thermochemistry alone cannot account for the steady gradation in activation energy along the series 7a, 7b and 7c. It is interesting to speculate on the cause of the wide variation in activation energy for these reactions. Presumably it arises from differences in the repulsion energies upon close approach of the reacting particles, chlorine being the least repelled and methyl the most. If we are to retain the idea that the "transition state" in these reactions is a fairly localized affair and that the methane molecule does not fly apart when a chlorine atom passes nearby, we must accept that the chlorine atom can approach very close to the methane molecule without any marked repulsion. We imagine that this is only possible because the free electron on the chlorine atom has a significant attraction for the electrons in the methane molecule. Therefore, we should expect that the greater the electroaffinity of the singly occupied orbital, the easier the close approach of the two centers would be. If the methyl radical is flat, it should have an electroaffinity of about 6 e.v.²⁰; the values for the hydrogen and chlorine atoms are 7.2 and 9.5 e.v., respectively.²¹ Thus the relative values of the activation energies of reactions 7a, 7b and 7c can be understood in terms of the electroaffinities of the approaching particles. It seems that we can distinguish at least two factors which govern the activation energy of reaction 7 for a constant RH, these being the thermochemistry of the reaction and the electroaffinity of the abstracting particle.

In spite of the difficulties in analysis without resort to mass-spectrometric techniques, we feel that the numerical results presented here are essentially correct: the further exploitation of the competitive method using physicochemical methods of analysis is not feasible. But with a mass-spectrometer available, the range of substances investigated could be considerably extended, the accuracy improved, and interesting results on the relative rates of reactions 2 and 4 could be collected.

MANCHESTER, ENGLAND

(20) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, in press.

(21) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

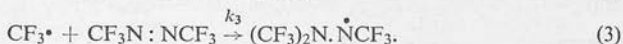
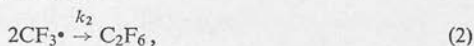
THE REACTIONS OF TRIFLUOROMETHYL RADICALS

THE REACTIONS OF TRIFLUOROMETHYL RADICALS

BY G. O. PRITCHARD,* H. O. PRITCHARD,* H. I. SCHIFF †
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(a) The photolysis of hexafluoroazomethane yields trifluoromethyl radicals which both combine (2) and add to the N:N bond (3):



In the presence of a hydrogen-containing compound, RH, CF_3H is produced by (1):



So many of the radicals add to the parent compound (3) that k_1 cannot be accurately compared with k_2 ; the rate of this addition is given by

$$k_3/k_2^{\frac{1}{2}} = 3.0 \times 10^3 \exp \left[- (3,500 \pm 200)/RT \right] \text{ mole}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-1}$$

between -70° and 100°C .

(b) The rate constants k_1 for a number of compounds have been compared with k_5 ,



by measurement of the relative rates of production of CF_3H and CF_3D in a photolytic system containing RH, deuterium and hexafluoroazomethane. A_1 and E_1 have been determined from the Arrhenius equations. It is found that E_1 is in general 2 or 3 kcal/mole lower than the activation energy for the corresponding methyl radical reactions.

(c) The heat of the reaction $\text{CF}_3\cdot + \text{CH}_4 \rightarrow \text{CF}_3\text{H} + \text{CH}_3\cdot$ has been derived from the activation energies of the forward and reverse reactions, leading to the value

$$D(\text{CF}_3 - \text{H}) = D(\text{CH}_3 - \text{H}) - 0.5 \text{ kcal/mole}.$$

In recent years much work has been done to determine the Arrhenius parameters of reactions involving atoms and small free radicals. Most progress has been made in the determination of the rate constants of those reactions in which the atom or radical abstracts a hydrogen atom from a hydrogen-containing compound—usually a hydrocarbon. The reactions of methyl radicals¹ have been very fully investigated. Less is known about the reactions of chlorine,² hydrogen and bromine atoms and ethyl radicals.^{3,4} The ultimate object of much of this work has been to discover the factors determining the rates of reactions through the study of many series of similar reactions and the correlation of their rates with the thermodynamic and structural properties of the reactants. Particular interest attaches to the reactions of the trifluoromethyl radical because (as is shown in the present work) the $\text{CF}_3\text{—H}$ bond is almost the same strength as the $\text{CH}_3\text{—H}$ bond, though the $\text{CF}_3\cdot$ radical is probably much more electro-negative than the $\text{CH}_3\cdot$ radical. Also, $\text{CF}_3\cdot$ has a much higher moment of inertia (and hence rotational entropy) than $\text{CH}_3\cdot$. Consequently, the entropy change occurring in the symmetrical dissociation of C_2F_6 is much greater than that which occurs when C_2H_6 dissociates, so that either the Arrhenius A factors for the two

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dissociations or the two recombinations (or possibly both) must be very different. No direct evidence on this point has been obtained in the course of the present work, but it should be borne in mind when the A factors of $\text{CF}_3\cdot$ metathetical reactions are considered.

It might be expected that, by analogy with the reactions of methyl radicals, in the presence of a saturated hydrocarbon RH , trifluoromethyl radicals would undergo the two competing reactions



and



The rates of formation of CF_3H and C_2F_6 respectively would then be given by the two expressions:

$$R_{\text{CF}_3\text{H}} = d[\text{CF}_3\text{H}]/dt = k_1[\text{CF}_3\cdot][\text{RH}]$$

and

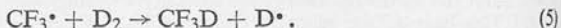
$$R_{\text{C}_2\text{F}_6} = d[\text{C}_2\text{F}_6]/dt = k_2[\text{CF}_3\cdot]^2,$$

whence

$$k_1/k_2^{1/2} = R_{\text{CF}_3\text{H}}/R_{\text{C}_2\text{F}_6}^{1/2}[\text{RH}].$$

The temperature coefficient of this rate ratio is the difference in activation energies $E_1 - \frac{1}{2}E_2$ and the pre-exponential factor is $A_1/A_2^{1/2}$. The results obtained in this research bear out this expectation.

Hexafluoroazomethane was chosen as a source of trifluoromethyl radicals, both because it is fairly simple to prepare and because its photolysis can be effected by visible (blue) light; thus the range of compounds RH is not restricted only to compounds which do not absorb in the near ultra-violet. First, it was necessary to investigate the photolysis of hexafluoroazomethane which is described in section (a); next, an attempt was made to determine $k_1/k_2^{1/2}$ by analysis for CF_3H and C_2F_6 formed during the photolysis of hydrocarbon + hexafluoroazomethane mixtures, but because of inherent difficulties, this approach was abandoned in favour of a method yielding relative rate constants by the comparison of the rate of a series of reactions of type 1 with reaction (5),



This part of the work is described in section (b), followed by the determination of the $\text{CF}_3\text{—H}$ bond strength in section (c).

EXPERIMENTAL

MATERIALS.—Hexafluoroazomethane was prepared by heating ICN and IF_5 in a steel bomb at 130 to 140° C.⁵ The contents of the bomb were then pumped into a trap containing solid KOH at liquid nitrogen temperature where any HF and most of the free iodine produced in the reaction were absorbed; the product could then be handled conveniently in all glass apparatus. The major impurity was stated by Ruff and Willenberg⁵ to be *bistrifluoromethylamine* $(\text{CF}_3)_2\text{NH}$ (which probably arises from the presence of HF in the IF_5); it was removed by shaking the gas first with dilute hydrochloric acid, which decomposes the impurity to HF , HOCN and CO_2 , and then with dilute sodium hydroxide solution to remove these acid products and any residual iodine. The product was dried over P_2O_5 and stored in the dark at liquid nitrogen temperature.

Mass spectrographic analysis showed this product to be essentially $\text{CF}_3\text{N}:\text{NCF}_3$, containing some CF_3I , SiF_4 and small amounts of hydrocarbons up to and including C_5 . Photolysis of this material at 25° C yielded a mixture of C_2F_6 and CF_3H containing nearly 40 % CF_3H , showing that the hydrogen-containing impurities were extremely susceptible to $\text{CF}_3\cdot$ radical attack. Further purification was effected by repeated fractional distillation at temperatures in the range -120 to -155° until photolysis yielded a C_2F_6 fraction containing only 1.3 % CF_3H . This material was considered to be sufficiently pure for the purposes of the present investigation; its molecular weight was found to be 168 (after correction for deviation from the gas laws) and the only impurity detectable in the mass spectrum was a trace of CF_3I .

Hexafluoroazomethane is a faintly greenish gas; b.p. -31.6° ; Ruff and Willenberg gave the vapour pressure as

$$\log_{10} P \text{ (in mm)} = (-1196/T) + 7.832,$$

and our measurements are in excellent agreement with this equation in the temperature range -35 to -80° . They stated that the gas decomposes in the presence of mercury giving $N_2 + C_2F_6$, but we have not confirmed this observation; the gas is stable in the dark, even in the presence of mercury, but is slowly decomposed by daylight. The gas exhibits a very intense absorption in the infra-red spectral region; the principal absorption lines and their relative intensities are given in table 1. The very weak triplet near 2800 cm^{-1} could be due to C—H vibrations, but their general disposition suggests that it is more likely to be a combination band (we are indebted to Dr. G. D. Meakins for discussion on this point); furthermore, a number of detailed searches of the mass spectrum have failed to reveal the presence of any hydrogen atoms in the product.

TABLE 1.—INFRA-RED ABSORPTION SPECTRUM OF HEXAFLUOROAZOMETHANE

(cm^{-1})	intensity	(cm^{-1})	intensity	(cm^{-1})	intensity
2950	v.w.	1860	w.	1084	s.
2850	v.w.	1825	v.w.	1079	s.
2782	w.	1773	w.	1072	s.
2470	m.	1667	v.w.	1034	m.
2250	v.w.	1581	m.	1025	m.
2202	m.	1562	m.	973	w.
2140	m.	1532	w.	949	m.
2072	m.	1458	m.	878	m.
2022	m.	1404	s.	744	m.
1955	w.	1274	v.s.	739	m.
1915	v.w.	1210	v.s.	733	m.

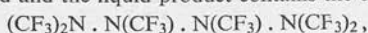
Note.—Spectra were observed with pressures of 280, 14 and 1 mm Hg in a 10 cm absorption cell: v.w. indicates that the absorption can only be detected at 280 mm, whereas v.s. indicates 50-80 % absorption at 1 mm pressure; w., m., and s. denote intermediate intensities.

Deuterium was prepared by electrolysis of a saturated solution of Na_2SO_4 in 99.7 % D_2O , and was freed from O_2 and D_2O by passing through a quartz tube containing boiling sodium; mass spectrometer analyses yielded $D_2 = 96.5\%$, $HD = 3.5\%$. Hydrogen was obtained from a cylinder and was purified using a palladium thimble. The aliphatic hydrocarbons used were standard samples supplied by the Chemical Research Laboratory, Teddington; acetone and benzene were of A.R. grade and the toluene was a pyrolyzed sample. Hexadeuteroacetone was kindly given to us by the National Research Council, Ottawa.

APPARATUS AND PROCEDURE.—Most of the experiments were carried out using a 300 ml quartz reaction vessel which was isolated from the main vacuum system by a mercury cut-off. This vessel was enclosed in an electric furnace, whose temperature could be controlled to $\pm 2^{\circ}$ in the range 30 to 350° , and was irradiated with light from a high-pressure mercury lamp for periods of from 3 to 24 h. After irradiation, the contents of the reaction vessel were pumped out and separated by low-temperature fractional distillation; the volume of each fraction was measured before being removed from the apparatus for mass spectrometric analysis.

(a) THE PHOTOLYSIS OF HEXAFLUOROAZOMETHANE

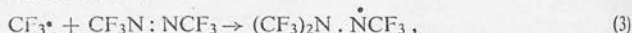
The photolysis of hexafluoroazomethane at room temperature and 5 cm pressure leads to the production of nitrogen, hexafluoroethane, a trace of fluoroform (as mentioned above) and a liquid product having a vapour pressure of 20-30 cm at room temperature (20°). This was shown by mass spectrographic analysis to be $(CF_3)_2N \cdot N(CF_3)_2$; presumably it is formed by the addition of CF_3^{\bullet} radicals to the N:N double bond in hexafluoroazomethane. The relative volumes of products in one run at room temperature were N_2 9.8, C_2F_6 1.9, CF_3H 0.025 and $(CF_3)_4N_2$ 7.8; the almost exact material balance shows that all the CF_3^{\bullet} radicals are accounted for and that about 80 % of them are lost by addition to the parent compound. At higher temperatures the material balance is not maintained and the liquid product contains the compound



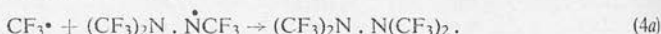
our identification of these liquid products is based on mass spectrometric evidence, and is confirmed in a paper by Dacey and Young⁶ which appeared after this work was completed. No evidence was found for the formation of any CF_4 up to the highest temperatures used (350°); however, above about 150° , small amounts of CO_2 and SiF_4 were produced by the attack of CF_3^\bullet radicals on the quartz. A similar attack was found by Ayscough and Emeléus⁷ in the pyrolysis of $\text{As}(\text{CF}_3)_3$ and $\text{Sb}(\text{CF}_3)_3$, but Sieger and Calvert⁸ did not find it in their photolysis experiments with trifluoroacetone.

The kinetics of the addition reaction were studied in a subsidiary apparatus: samples of hexafluoroazomethane were sealed in a 170 ml Pyrex cylinder which was placed in a thermostatted air-space whose temperature could be maintained constant to $\pm 1^\circ\text{C}$ in the range from room temperature to -70°C . After illumination with light from a mercury vapour lamp (for a period of time sufficient to decompose about 5% of the azo-compound), the reaction vessel was re-attached to the main apparatus, the seal broken, and the contents analysed.

In these experiments performed at or below room temperature, the only products were N_2 , C_2F_6 and $(\text{CF}_3)_2\text{N} \cdot \text{N}(\text{CF}_3)_2$; we have assumed that the production of perfluorotetramethylhydrazine takes place by



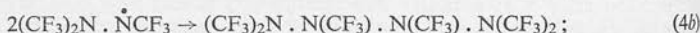
which is rate-determining, followed by the fast reaction



Thus, the rate constant for the addition is given by

$$k_3/k_2^{\frac{1}{2}} = R_{(\text{CF}_3)_2\text{N} \cdot \text{N}(\text{CF}_3)_2} / R_{\text{C}_2\text{F}_6}^{\frac{1}{2}} [\text{CF}_3\text{N} : \text{NCF}_3].$$

The Arrhenius plot of these results is given in fig. 1. A further point, obtained from experiments carried out (in the main apparatus) at 100°C also lies on this straight line; at this temperature some perfluorohexamethyltetrazine was formed, presumably by the reaction



from a knowledge of the drop in pressure during the reaction and the total quantity of the liquid product, the extent of reaction (3) was obtained leading to the highest temperature point shown in fig. 1. Fitting these results to the Arrhenius equation leads to the expression

$$k_3/k_2^{\frac{1}{2}} = 3.0 \times 10^3 \exp [-(3,500 \pm 200)/RT] \text{ moles}^{-\frac{1}{2}} \text{ cm}^3 \text{ sec}^{-\frac{1}{2}}.$$

(b) THE REACTION OF CF_3^\bullet RADICALS WITH HYDROGEN-CONTAINING COMPOUNDS

In some earlier experiments, an attempt was made to compare the rates of reactions (1) and (2) by photolyzing hexafluoroazomethane in the presence of hydrocarbons and comparing the rates of formation of CF_3H and C_2F_6 . However, the extreme ease with which radicals were removed by reaction (3) so reduced the static concentration of CF_3^\bullet radicals that only minute amounts of C_2F_6 were formed, and it was only by extending the temperature range over at least 200°C that even approximate data about the relative activation energies of reactions (1) and (2) could be obtained.⁹ It was therefore decided to investigate only the relative reactivities of a series of compounds RH towards CF_3^\bullet radical attack; this was done by photolyzing about 2 cm of hexafluoroazomethane in the presence of about 10 cm of D_2 and sufficient RH to produce a reasonable ratio of CF_3D to CF_3H for analytical purposes. Thus the rates of a whole series of reactions were related to the rate of the reaction,



from a knowledge only of the ratio of RH and D_2 present, and the ratio of CF_3H to CF_3D produced. The latter ratio was determined mass-spectrometrically from the relative abundances of the CF_2H^+ and CF_2D^+ peaks, allowing for ^{13}C contributions and making the assumption that the cracking patterns and sensitivities of the two molecules are similar. (Should they differ slightly, this will reflect itself in the relative frequency factors, but the relative activation energies will remain unchanged.) A detailed set of results for the reaction with $\text{H}_2 + \text{D}_2$ mixtures is given in table 2 and fig. 2, and in fig. 3 the Arrhenius plots for a series of $\text{RH} + \text{D}_2$ mixtures are given. We considered it the purpose of this work to explore the whole field of CF_3^\bullet radical reactivity, and in consequence,

most of the Arrhenius plots are based on four or five points; the whole of this data is summarized in table 3 (together with some less reliable data on *isobutane*, benzene and toluene). For the purposes of calculating absolute values of $E_1 - \frac{1}{2}E_2$, we have chosen Ayscough, Polanyi and Steacie's result¹² for $\text{CF}_3^\bullet + \text{C}_2\text{H}_6$ as a standard and all the values given in table 3, with the exception of those for methane, are related to this determination; the corresponding rate factors for CH_3^\bullet radical reactions are also given in table 3 for comparison.

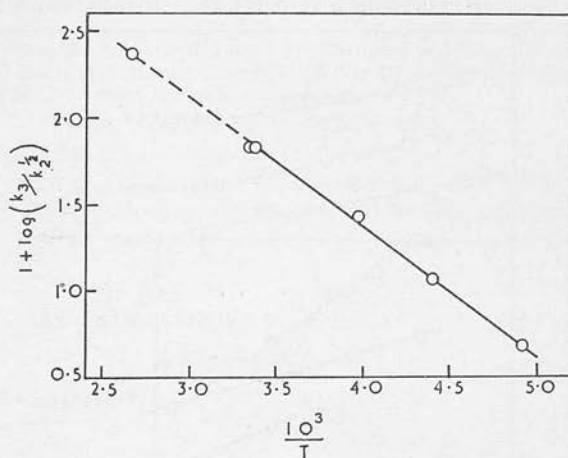


FIG. 1.

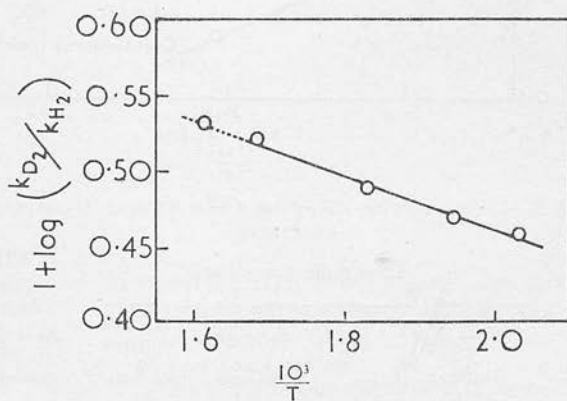


FIG. 2.

TABLE 2.—THE REACTION OF CF_3^\bullet RADICALS WITH HYDROGEN + DEUTERIUM MIXTURES

temp. °C	time (min)	pressure D_2 (cm)	pressure H_2 (cm)	$\text{CF}_3\text{D}/[\text{CF}_3\text{H}]$	k_2/k_1
219	300	12.74	3.23	1.135	0.287
241	270	9.53	2.59	1.087	0.295
273	210	8.92	4.41	0.624	0.309
320	60	8.95	6.14	0.486	0.334
344	10	9.35	4.01	0.750	0.321
346	10	7.45	4.96	0.387	0.362

$$k_2/k_1 = \frac{d[\text{CF}_3\text{D}]/dt}{d[\text{CF}_3\text{H}]/dt} \frac{[\text{H}_2]}{[\text{D}_2]} = 0.69 \exp [-(860 \pm 80)/RT].$$

These and other results have been corrected for the fact that a proportion of the CF_3H arises from HD originally present in the D_2 ; the extent of this correction was estimated from a consideration of the results of Whittle and Steacie¹⁰ on the reactions $\text{CH}_3\cdot + \text{HD}$ and $\text{CD}_3\cdot + \text{HD}$. Also, in those runs carried out above 320°C , difficulty was encountered because hexafluoroazomethane decomposes ($\rightarrow \text{N}_2 + 2\text{CF}_3\cdot$) thermally (at 300°C the rate is equivalent to 10 % decomposition in 1 h¹¹): consequently, at 345°C an average had to be taken over two runs carried out using complementary mixing procedures (i.e. injection into reaction vessel in the order [substrate + H_2 + D_2] and [substrate + D_2 + H_2]).

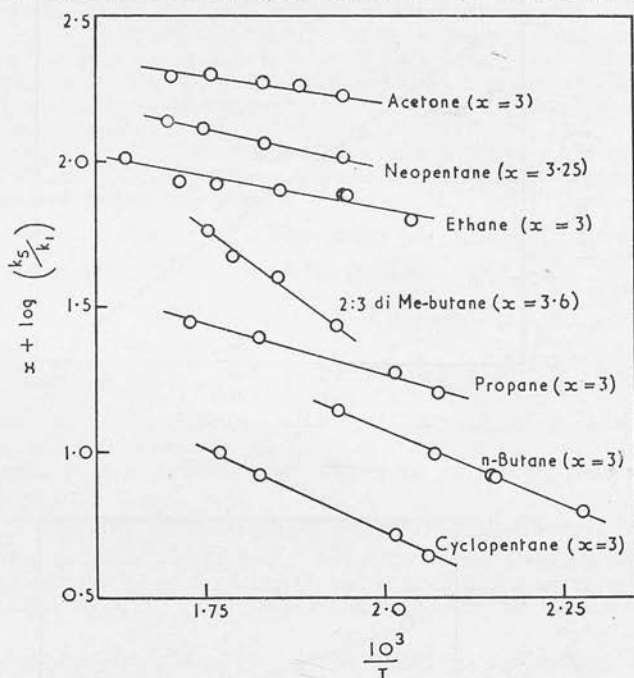


FIG. 3.

TABLE 3.—COMPARISON OF $\text{CF}_3\cdot$ AND $\text{CH}_3\cdot$ RADICAL H-ABSTRACTION REACTIONS

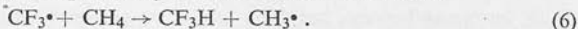
RH	$\text{CF}_3\cdot$ radical reactions				$\text{CH}_3\cdot$ radical reactions ^a	
	$E_5 - E_1$ kcal/mole	A_5/A_1	$E_1 - \frac{1}{2}E_2$ kcal/mole	$A_1/A_2^{\frac{1}{2}} \times 10^{-4}$ mole $^{-\frac{1}{2}}$ cm $^{\frac{3}{2}}$ sec $^{-\frac{1}{2}}$	$E_1 - \frac{1}{2}E_2$ kcal/mole	$A_1/A_2^{\frac{1}{2}} \times 10^{-4}$ mole $^{-\frac{1}{2}}$ cm $^{\frac{3}{2}}$ sec $^{-\frac{1}{2}}$
deuterium	—	—	9.7	5.8	11.8	(12.9)
hydrogen	0.86 ± 0.08	0.69	8.8	8.4	10.0	(21.8)
methane	—	—	10.3 ^b	9.7 ^b	~13	—
ethane	2.20 ± 0.50	0.62	7.5 ^b	9.4 ^b	10.4	2.8
neopentane	2.10 ± 0.20	0.47	7.6	12	10.0	3.0
propane	3.5 ± 0.5	0.60	6.2	9.7	—	—
n-butane	4.40 ± 0.10	0.97	5.3	6.0	8.3	1.6
cyclopentane	5.0 ± 0.2	0.81	4.7	7.2	8.3	3.6
isobutane	~6.7	(8.0)	(3.0)	(0.73)	7.6	1.5
2:3-diMebutane	8.0 ± 1.0	16.7	1.7	0.35	6.9	1.0
acetone	1.7 ± 0.5	0.85	8.0	6.8	9.7	6.0
benzene	~2	(1.0)	(7.7)	(5.8)	9.2	0.37
toluene	3.7 ± 1.0	1.30	6.0	4.5	8.3	2.1

^a methyl radical values from Trotman-Dickenson, ref. (1) and Whittle and Steacie, ref. (10).

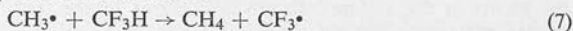
^b from Ayscough, Polanyi and Steacie, ref. (12).

(c) THE C—H DISSOCIATION ENERGY IN FLUOROFORM

It is impossible to understand the factors governing the rates of these CF_3^\bullet radical reactions without a knowledge of their thermochemistry. Before this investigation was undertaken, virtually nothing was known with any certainty about the strengths of bonds formed by the CF_3 -group, and in consequence, we have measured $D(\text{CF}_3\text{—H})$ by the classical kinetic method. We had previously shown⁹ that for the reaction



$E_6 - \frac{1}{2}E_2$ was in the range 9.5 ± 2 kcal/mole, and this has been confirmed by Ayscough, Polanyi and Steacie¹² who derived a more precise figure of 10.3 ± 0.5 kcal from experiments in which hexafluoroacetone was photolyzed in the presence of methane; a knowledge of the activation energy of the back reaction



is then sufficient to give $D(\text{CF}_3\text{—H})$ by the relationship,

$$D(\text{CH}_3\text{—H}) - D(\text{CF}_3\text{—H}) = E_6 - E_7.$$

Furthermore, it is now reasonably well established that the isotopic substitution of the

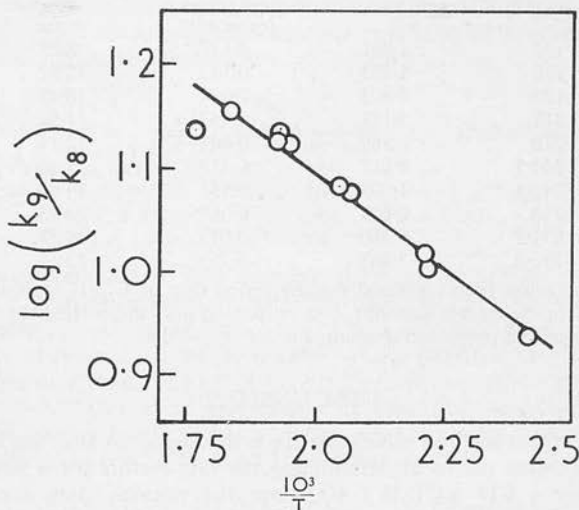


FIG. 4.

three hydrogen atoms in the methyl radical makes very little difference to its reactivity,^{10, 13} so that we may identify E_7 with E_8 , the activation energy of the process,



which is much more easily measured experimentally.

Mixtures of about 5 cm of 95 % acetone- d_6 and some 5-20 cm of fluoroform were photolyzed at temperatures in the range 140-290° C; the fraction of the products volatile at -195° C (i.e. CO, CD_4 and CD_3H) was separated off, and the ratio of $[\text{CD}_3\text{H}]/[\text{CD}_4]$ was determined mass-spectrometrically. In addition to reaction (8), the CD_3^\bullet radicals can undergo the reactions



Thus the rate of reaction (8) can be related to the known rate of reaction (9) by the expression

$$\frac{k_9}{k_8} = \frac{d[\text{CD}_4]/dt}{d[\text{CD}_3\text{H}]/dt} \frac{[\text{CF}_3\text{H}]}{[\text{CD}_3\text{COCD}_3]};$$

the results of ten experiments are listed in table 4 and the Arrhenius plot is shown in fig. 4, leading to the relation $k_9/k_8 = 75 \exp [-(1800 \pm 150)/RT]$ (the error quoted being the maximum deviation of the Arrhenius plot). The activation energy of reaction (9) is known relative to that of reaction (10) from work on the photolysis of acetone- d_6 by Whittle

and Steacie,¹⁰ and their value of $E_9 - \frac{1}{2}E_{10} = 11.6$ kcal/mole has been confirmed indirectly by McNesby and Gordon.¹³ Using these results, we have

$$E_6 = (10.3 + \frac{1}{2}E_2) \text{ and } E_7 = E_8 = (11.6 + \frac{1}{2}E_{10} - 1.8),$$

whence $D(\text{CF}_3\text{—H}) = D(\text{CH}_3\text{—H}) - 10.3 - \frac{1}{2}E_2 + 11.6 + \frac{1}{2}E_{10} - 1.8.$

$$= D(\text{CH}_3\text{—H}) - \frac{1}{2}E_2 + \frac{1}{2}E_{10} - 0.5 \text{ kcal/mole.}$$

E_{10} is known to be zero, but there have been numerous suggestions that because of the highly polar nature of the C—F bond, there may be a potential barrier to the combination of two $\text{CF}_3\cdot$ radicals and that E_2 may differ considerably from zero (see, e.g., Sieger and Calvert, ref. (8)); such arguments are fallacious as it can be shown that a potential barrier to combination will arise only when there is a change in multiplicity of one or more of the atoms in the system; in reaction (2) as in reaction (10), the multiplicities of all centres remain unchanged throughout the course of the combination process. Thus, if we assume that $D(\text{CH}_3\text{—H}) = 102.5 \pm 1$,¹⁴ we have $D(\text{CF}_3\text{—H}) = 102.0 \pm 2$ kcal/mole.

TABLE 4.—THE PHOTOLYSIS OF ACETONE- d_6 IN THE PRESENCE OF FLUOROFORM

temp. °C	$[\text{CF}_3\text{H}]/[\text{acetone-}d_6]$	$[\text{CD}_3\text{H}]/[\text{CD}_4]$ (corrected) *	k_9/k_8
142	1.091	0.127	8.56
178	1.433	0.143	10.02
180	0.903	0.087	10.41
211	3.123	0.262	11.92
216	0.589	0.049	12.12
244.5	3.517	0.258	13.63
245.5	1.803	0.133	13.56
246	0.639	0.048	13.43
271.5	0.760	0.053	14.31
292.5	3.462	0.253	13.68

* This column has been corrected for the proportion of CD_3H formed from the H atom impurity in the heavy acetone; this correction was approximately constant over the whole temperature range and amounted to 0.071 ± 0.006 .

DISCUSSION

The competitive method which we have developed in this work provides a simple and accurate means of determining the rate factors for a whole series of reactions, $\text{CF}_3\cdot + \text{RH} \rightarrow \text{CF}_3\text{H} + \text{R}\cdot$, once the relevant data are known for one such reaction of this type. The only difficulty arises in the preparation of deuterated substandards of sufficient isotopic purity. For example, we have not been able to study the methane reaction by this method because methane is so unreactive that as much CF_3H would be formed from reaction with the HD impurity in the D_2 as from reaction with the methane itself. The correction to be applied would then be too large for the results to be of any value. Some difficulty was experienced also at the other end of the reactivity scale (i.e. with 2:3-dimethylbutane and with isobutane) because they are so much more reactive than D_2 : this difficulty can, however, be overcome in principle by the use of a deuterated substandard of intermediate reactivity, for example, C_2D_6 ; we have not performed any experiments of this kind.

The results obtained for the competition between H_2 and D_2 (see table 2 and fig. 2) are of particular interest. The activation energy for $\text{CF}_3\cdot$ radical attack on D_2 is greater than for H_2 by an amount which is approximately half of the difference in zero-point energy between these molecules, and the ratio of the frequency factors is 0.69, which is almost exactly equal to the ratio of the relative collision numbers (i.e., $2^{-\frac{1}{2}}$) for the two reactions. In view of this result, it seems unlikely that the activation energies for the corresponding $\text{CH}_3\cdot$ radical reactions could differ by 1.8 kcal (cf. the values of 11.8 and 10.0 given by Whittle and Steacie¹⁰); note, however, that Whittle and Steacie also found 11.1 kcal for the activation energy for $\text{CD}_3\cdot + \text{H}_2$ which seems more reasonable in comparison

with the activation energy for $\text{CH}_3^\bullet + \text{D}_2$. It can be seen by a comparison of columns 4 and 6 of table 3 that in general the reactions of CF_3^\bullet radicals have activation energies about 2 or 3 kcal less than the corresponding CH_3^\bullet radical reactions. (This, too, appears to be true for the addition to the N:N double bond, if we compare the value of 3.5 kcal obtained in this work for



with that of 6.5 obtained by Jones and Steacie¹⁵ for $\text{CH}_3^\bullet + \text{CH}_3\text{N}:\text{NCH}_3$). On the other hand, the frequency factor ratios $A_1/A_2^{1/2}$ for the two sets of reactions are in general very similar but it is difficult at this stage to comment further on this similarity because we cannot quote with any certainty the relative frequency factors for the combination reactions of the two radicals.

The fact that the activation energies for CF_3^\bullet radical reactions are lower than those for CH_3^\bullet radicals is, however, readily understandable in terms of the idea that activation energies and electronegativities are related.² It so happens that reaction (6) is virtually thermoneutral, making possible a direct comparison with three other reactions in which a hydrogen atom is abstracted from the methane molecule. In table 5, the relevant data on these reactions, all of which are thermo-neutral to within the experimental error, are presented.

TABLE 5

reaction	activation energy, E (kcal/mole)	Mulliken electronegativity, χ (eV)
$\text{Cl}^\bullet + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3^\bullet$	3.9	9.5
$\text{H}^\bullet + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3^\bullet$	10.0	7.2
$\text{CF}_3^\bullet + \text{CH}_4 \rightarrow \text{CF}_3\text{H} + \text{CH}_3^\bullet$	10.3	> 6
$\text{CH}_3^\bullet + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_3^\bullet$	~ 13	~ 6

It is not suggested that all four reactions form one series (i.e. one cannot use the values of E to derive a value for χ for the CF_3^\bullet radical): however, it is clear that the increase in χ on going from H^\bullet to Cl^\bullet is accompanied by a substantial decrease in E ; likewise, on going from CH_3^\bullet to CF_3^\bullet (which is known to be much more electronegative than the methyl radical¹⁶) there is again a significant drop in the value of E . This effect will be equally operative throughout the whole series of CF_3^\bullet reactions studied, so that they all must have activation energies slightly lower than the corresponding CH_3^\bullet radical reactions.

We wish to thank Mr. V. W. Rowlands of the Widnes Laboratory, I.C.I. General Chemicals Division, Widnes, for performing a number of mass-spectrometer analyses concerned with establishing the purity of the hexafluoroazomethane and with the identification of the products of its photolysis. The work was carried out while one of us (G. O. P.) was in receipt of a D.S.I.R. maintenance grant.

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¹⁰ Whittle and Steacie, *J. Chem. Physics*, 1953, 21, 993.

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¹³ McNesby and Gordon, *J. Amer. Chem. Soc.*, 1954, 76, 1416.

¹⁴ Roberts and Skinner, *Trans. Faraday Soc.*, 1949, 45, 339.

¹⁵ Jones and Steacie, *J. Chem. Physics*, 1953, 21, 1018.

¹⁶ Pritchard and Skinner, *Chem. Rev.*, 1955, 55, 745.

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749. *The Thermal Decomposition of cyclopentyl Bromide.*

By S. J. W. PRICE, R. SHAW, and A. F. TROTMAN-DICKENSON.

The thermal decomposition of *cyclopentyl* bromide into *cyclopentene* and hydrogen bromide has been studied in a static system at temperatures between 300° and 360° c. The decomposition is homogeneous and obeys first-order kinetics in its early stages; the rate constant is given by

$$k = 10^{11} \exp (-41,400/RT) \text{ sec.}^{-1}$$

The elimination of hydrogen bromide is probably a molecular process, as the addition of *cyclohexene* has no effect upon the rate.

DURING the past few years the thermal decomposition of many aliphatic bromides has been investigated, chiefly by Maccoll and his collaborators.^{1,2} The majority of these bromides, in the presence of an inhibitor, decompose by a four-centre molecular elimination mechanism into hydrogen bromide and an olefin. One of the compounds which has been found to react in this way is *cyclohexyl* bromide.³ The rate constant for its decomposition is given by the Arrhenius equation

$$k = 10^{13.5} \exp (-46,100/RT) \text{ sec.}^{-1}$$

The investigation of the decomposition of *cyclopentyl* bromide was undertaken in the hope that a knowledge of the rate factors, *A* and *E* in the Arrhenius equation, would throw light on the features of molecules which determine the rates of molecular elimination reactions. In particular, it was thought that the different degrees of flexibility of the carbon rings might influence the rates.

EXPERIMENTAL

Materials.—The *cyclopentyl* bromide was a gift from the Michigan Chemical Company. It was degassed and purified by bulb-to-bulb distillation. No significant quantities of impurity could be detected by vapour-phase chromatography. The *cyclohexene*, which was similarly degassed, was freed from peroxides by shaking with acid ferrous sulphate solution.

Apparatus.—The decomposition was studied in a bulb of 385 c.c. capacity attached to a conventional vacuum-system by tubing with a total dead space of approx. 13 c.c. The bulb was contained in a mercury-vapour jacket, whose temperature could be readily controlled by varying the pressure under which the mercury boiled. The temperature of the jacket was determined by reference to standard tables of the vapour pressure of mercury. The reaction was studied by following the change in pressure in the reaction vessel on a mercury manometer. It was found that the hydrogen bromide formed did not appreciably attack the mercury during a run, for the reaction vessel was separated from the manometer by about 30 cm. of 2-mm. capillary tubing.

Procedure.—Runs were started by admitting a suitable quantity of the bromide to the reaction vessel from a storage bulb; in some runs a quantity of *cyclohexene* was also added. Readings of the pressure in the vessel were then recorded at convenient intervals. At the end of some of the runs the quantity of hydrogen bromide formed was determined analytically. It was found that inexplicably erratic and high results were usually obtained when the unseparated products were titrated with alkali, so the following procedure was adopted. First, the products were condensed in a side bulb, and the hydrogen bromide was separated by low-temperature distillation. Its amount was then determined by pressure measurements and by dissolving the gas in water and titrating the solution for hydrogen and halide ions. The results of the three determinations were always in excellent agreement. When a proper correction was made for the dead space it was found that the analytical results agreed well with degrees of decomposition deduced from the pressure measurements.

Rate constants were determined in the usual way from first-order plots of the logarithms of the pressure changes against time. The logarithmic plots were strictly linear for the first third of the reaction but thereafter tended to curve. The curvature was probably caused by the increasing importance of the back reaction. The rate constants for a few runs were calculated from the full expression for a first-order reaction opposed by a second-order reaction. The rate constants obtained in this way differed by only about 10% from those calculated by applying the equation for a simple first-order reaction to the observations made during the first third of the decomposition. All the rate constants reported here were determined by the less tedious procedure.

All runs showed short induction periods. Their lengths corresponded roughly to the time needed for 2–3% of the bromide to decompose. The presence of *cyclohexene* appeared to shorten the induction periods slightly.

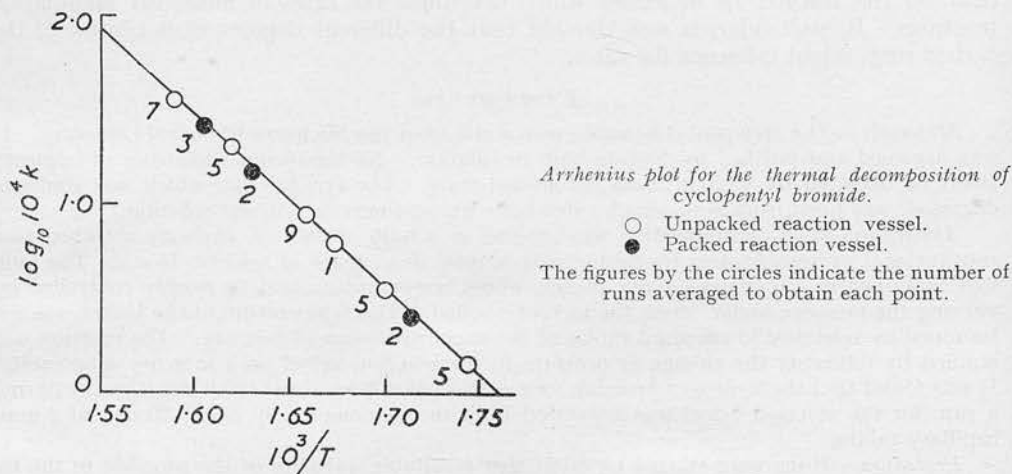
RESULTS and DISCUSSION

Preliminary runs in a clean-walled reaction vessel gave first-order rate constants which decreased slowly but steadily from run to run. Maccoll and his collaborators observed similar behaviour with other bromides and attributed the effect to heterogeneous processes. They therefore seasoned their reaction vessels by decomposing allyl bromide in them. This remedy proved effective for *cyclopentyl* bromide also. It was used after any occasion on which air had been admitted to the reaction vessel. Incidentally, Maccoll's rate constant⁴ for the decomposition of allyl bromide was confirmed.

The first-order nature of the decomposition was demonstrated by studying it with various initial pressures of *cyclopentyl* bromide. The results obtained for a typical series of runs, all corrected to 356.5°, were as follows:

Initial pressure (mm.)	38.0	49.6	59.6	79.5	94.0	105.0	107.5
$10^3 k$ (sec. ⁻¹)	3.48	3.48	3.39	3.66	3.53	3.80	3.78

The very small effect on the rate constant of the addition of *cyclohexene* can be seen from the following Table, in which the observed rate constants are compared with those



calculated from the Arrhenius equation. The variations in the rates are of the same order as the experimental error.

<i>cycloHexene</i> (mm.)	20.0	30.0	10.0	9.0	40.0
<i>cycloPentyl</i> bromide (mm.)	60.0	72.5	64.0	48.2	38.0
Temp.	300.7°	315.2°	331.3°	344.5°	365.5°
k (obs.)/ k (calc.)	1.05	0.95	1.02	0.98	0.91

Seven runs were carried out with the reaction vessel packed with Pyrex tubing so that the surface/volume ratio was increased from 0.9 to 2.0 cm.⁻¹. The results of these runs are distinctively plotted alongside the other results in the Figure. It can be seen that there is no evidence for any heterogeneous contribution to the reaction in an aged vessel.

The results of all the runs are shown on an Arrhenius plot in the Figure. The Arrhenius equation was derived by a least-squares treatment of the results for all the individual runs. The results are best expressed by the equation :

$$k = 10^{11.9} \exp (-41,400/RT) \text{ sec.}^{-1}$$

Our experiments indicate that this is the rate constant for the homogeneous gas-phase molecular elimination of hydrogen bromide from *cyclopentyl* bromide.

The rate constant for this decomposition at 380° (0.010 sec.⁻¹) is very slightly greater than that (0.008 sec.⁻¹) for the similar decomposition of *cyclohexyl* bromide. This conclusion is of interest in view of a recent important suggestion⁵ that the rate constants for the molecular elimination of hydrogen bromide from aliphatic bromides should run parallel to the rate constants for the elimination of bromide ions from the bromides by the S_N1 mechanism. No measurements on the rates of the S_N1 reactions of *cyclopentyl* and *cyclohexyl* bromide have been reported. It has been found,⁶ however, that the S_N1 reaction of 1-methylcyclopentyl chloride in 80% aqueous ethanol at 25° is 125 times more rapid than the corresponding reaction of 1-methylcyclohexyl chloride. Evidently the parallelism between the rates of the S_N1 reactions and the molecular eliminations breaks down in this instance. Probably the cause is the different natures of the strains in the two types of transition states.

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THE REACTIONS OF CHLORINE ATOMS—A TEST OF THE TRANSITION STATE THEORY

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Received March 9, 1956

The relative A factors for reactions of the type $\text{Cl} + \text{RH} = \text{HCl} + \text{R}$ have been calculated on the assumptions of the transition state theory. A comparison of these values with the accurate experimental data reveals considerable discrepancies.

The transition state theory of chemical kinetics has been applied with fair success to the calculation of the order of magnitude of the Arrhenius A factors of bimolecular reactions.¹ Little more can however be claimed for two reasons: firstly, doubtful assumptions as to the configurations of the activated complexes had to be made which led to considerable uncertainty in the calculated values, and secondly, experimental results of sufficient accuracy to sustain an unambiguous test were not available. The usual errors in the measurement of activation energies of these reactions were, under the most favorable conditions, of the order of ± 300 cal./mole. The corresponding error in the A factor is then $10^{\pm 0.2}$ (about $\pm 60\%$).

In the present paper, relative A factors calculated from transition state theory are compared with those determined experimentally by us^{2,3} for the competitive reactions of chlorine atoms with several hydrocarbons. Calculated A factor ratios are also given for a number of reactions which have

not yet been studied but which we hope to investigate in due course. These reactions of chlorine atoms offer a number of advantages for such a study. In the first place there is much less doubt about the configuration of the activated complexes in reactions of atoms than in the corresponding reactions of free radicals, there being no uncertainty about the free rotation of the radical in the former case. Secondly, the activation energies of the reactions are low and may therefore be measured with very small absolute errors (although the percentage error will be of the usual magnitude). It may furthermore be assumed that in such cases the bond lengths C-H-Cl will vary little from complex to complex and that the C-H and C-Cl bond lengths will be only slightly longer than those in normal molecules. Thirdly, by employing a competitive technique, relative A factors can be determined with unusual precision. In the most favorable cases relative activation energies have been measured to within 30 cal./mole giving relative A factors to within 5%.

These relative A factors can therefore provide a stringent test of the transition state theory since not only can they be measured experimentally with

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high precision but they may also be calculated with high accuracy making use of fewer assumptions than are required in the calculation of absolute values.

According to transition state theory the relative A factors for the competitive reaction of chlorine atoms with methane and ethane are given by the equation

$$\frac{A_{\text{CH}_4}}{A_{\text{C}_2\text{H}_6}} = \frac{[\phi_{\text{CH}_4\text{Cl}}^{\text{tr}} \phi_{\text{CH}_4\text{Cl}}^{\text{vib}} \phi_{\text{CH}_4\text{Cl}}^{\text{rot}}] / [\phi_{\text{CH}_4}^{\text{tr}} \phi_{\text{CH}_4}^{\text{rot}} \phi_{\text{CH}_4}^{\text{vib}}]}{[\phi_{\text{C}_2\text{H}_6\text{Cl}}^{\text{tr}} \phi_{\text{C}_2\text{H}_6\text{Cl}}^{\text{vib}} \phi_{\text{C}_2\text{H}_6\text{Cl}}^{\text{rot}}] / [\phi_{\text{C}_2\text{H}_6}^{\text{tr}} \phi_{\text{C}_2\text{H}_6}^{\text{rot}} \phi_{\text{C}_2\text{H}_6}^{\text{vib}}]} \\ = \exp \left[\frac{1}{R} (\Delta S_{\text{CH}_4}^{\text{tr}} - \Delta S_{\text{C}_2\text{H}_6}^{\text{tr}} + \Delta S_{\text{CH}_4}^{\text{rot}} - \Delta S_{\text{C}_2\text{H}_6}^{\text{rot}} + \Delta S_{\text{CH}_4}^{\text{vib}} - \Delta S_{\text{C}_2\text{H}_6}^{\text{vib}}) \right]$$

where the partition functions, denoted by ϕ 's, are measured from the ground state of the parent molecule and of the complex, respectively. The activation energy appropriate to these theoretical A factors is therefore the activation energy at absolute zero which may be denoted ΔE_0° . The ΔS values are the entropies of activation appropriate to the translational, rotational and vibrational degrees of freedom. In the above expression for the A factors the transmission coefficients have been omitted, and the symmetry numbers are taken to be included in the rotational partition functions. If the partition functions are evaluated without the symmetry numbers the values for the A factors are those for individual hydrogen atoms. Denoting such factors by A' the above equation can be written

$$\frac{A'_{\text{CH}_4}}{A'_{\text{C}_2\text{H}_6}} = \left\{ \frac{M_{\text{CH}_4\text{Cl}}/M_{\text{CH}_4}}{M_{\text{C}_2\text{H}_6\text{Cl}}/M_{\text{C}_2\text{H}_6}} \right\}^{3/2} \times \\ \left\{ \frac{(ABC)_{\text{CH}_4\text{Cl}}/(ABC)_{\text{CH}_4}}{(ABC)_{\text{C}_2\text{H}_6\text{Cl}}/(ABC)_{\text{C}_2\text{H}_6}} \right\}^{1/2} \times \exp \left[\frac{1}{R} (\Delta S_{\text{CH}_4}^{\text{tr}} - \Delta S_{\text{C}_2\text{H}_6}^{\text{tr}}) \right]$$

where M 's are the molecular weights of the various substances and the product (ABC) is the product of the moments of inertia about the three principal axes of the molecules. While the masses are known exactly, the values of (ABC) are not known with the same precision because of the slight uncertainty (probably less than 0.2 Å.) as to the C-H-Cl distances. Values of (ABC) can however be calculated to any degree of accuracy once a configuration has been accepted. Since any error in the C-H-Cl distances will affect the (ABC) 's of all complexes in the same sense and roughly in the same proportion, any error of choice will largely cancel out. There are three likely sources of error in comparing the calculated values with the experimental ones. The calculation of the vibrational entropy term is not possible with any certainty. It will however almost certainly be small. The vibrational entropies of methane and ethane are both less than 1 e.u. and the vibrational entropies of activation will therefore be much smaller than 1 e.u. Differences in vibrational entropies of activation as between say methane and ethane will be even smaller and probably not greater than ± 0.1 e.u. The vibrational term which might at first sight appear to result in large uncertainty in the calculation of the theoretical A factor should not therefore contribute more than about $\exp 0.1/R$, that is, about 5% uncertainty.

In these calculations the contributions from internal rotations in the parent molecules and the

complexes have been neglected. The appropriate allowance may readily be made only in the simplest cases where the rotators are symmetrical tops. In the case of ethane, for example, the contribution to the entropies of the parent and the complex due to free internal rotation are, ignoring the symmetry factor, 5.06 and 5.66 e.u., respectively. An error of about 30% may therefore be introduced in the particular case of ethane/methane by ignoring internal rotation. For higher homologs the contributions due to changes in internal rotation will be smaller than this. In the cases considered we are moreover concerned with restricted rotation rather than free rotation, and the effect of neglecting rotations is thus further reduced.

Lastly, there is likely to be a discrepancy between the theoretical and experimental A factors resulting from the fact that the experimental activation energy and the theoretical activation energy differ according to the equation

$$\Delta E_{\text{exp}} = \Delta E_0^\circ + \int_0^T \Delta C_v dT$$

giving

$$A_{\text{exp}} = A_{\text{calc}} \exp[(\int \Delta C_v dT)/RT]$$

The difference in ΔC_v for two similar reactions will however be very small since the translational and rotational specific heat changes will be identical for the two reactions and only the changes in vibrational specific heats will be important. As with the vibrational entropy contributions, these will be very small indeed.

We therefore conclude that the major factors influencing the relative A factors for two similar reactions are the changes in the translational and rotational entropies. Errors of up to some 5% are introduced by ignoring the vibrational contributions, and rather more by ignoring internal rotation. The latter is however never likely to be more than about 20%, even in an extreme case such as the comparison of the chlorinations of methane and ethane.

The details of the calculations are given below and a summary of the results appears in Table I. It already has been shown² that A factors of the right order of magnitude may be calculated for these chlorination reactions so that considerable interest attaches to the much more accurate values found for the relative A factors. These are given in Table II where they are compared with the experimentally determined values. Examination of the table reveals that the simple transition state theory predicts only approximately the relative A factors and that the discrepancy between the calculated and the experimental values is in the sense that too large an A factor is predicted for the lighter relative to the heavier molecules except in the indirect comparison of neopentane with isobutane where the mass difference is relatively small. These discrepancies (factors of up to ten) are well without both experimental error and any reasonable estimate of the theoretical error in our calculations. They may possibly be resolved in terms of transmission coefficients which we have neglected, but as yet no general method has been suggested by which such allowance might be made. The calculations show clearly the limits of the application of the simple transition state theory, and

TABLE I
TRANSLATIONAL AND ROTATIONAL ENTROPIES

Compound	S_{trans}	$\text{Log}_{10} \frac{ABC^a}{A^3}$	σ	S_{rot}
Cl	36.6	0	..	0
H ₂	28.1	1.68 ^b	2	4.1
H ₂ -Cl	36.8	0.89 ^b	1	11.0
CH ₄	34.3	1.56	12	10.3
CH ₃ -Cl	37.8	4.29	3	19.3
C ₂ H ₆	36.1	3.62	18	14.2
C ₂ H ₅ -Cl	38.9	5.78	3	22.7
C ₃ H ₈	37.2	4.84	18	17.0
C ₃ H ₇ cond. ^c	37.2	4.65	18	16.5
<i>p</i> -C ₃ H ₇ -Cl (a)	39.0	6.36	3	24.0
<i>p</i> -C ₃ H ₇ -Cl (a) cond.	39.0	6.26	3	23.8
<i>p</i> -C ₃ H ₇ -Cl (b)	39.0	6.35	3	24.0
<i>p</i> -C ₃ H ₇ -Cl (b) cond.	39.0	6.31	3	23.9
<i>s</i> -C ₃ H ₇ -Cl	39.0	6.47	9	22.1
<i>s</i> -C ₃ H ₇ -Cl cond.	39.0	6.43	9	22.0
iso-C ₄ H ₁₀	38.1	5.76	81	16.1
iso-C ₄ H ₁₀ cond.	38.1	5.46	81	15.4
<i>p</i> -iso-C ₄ H ₁₀ -Cl (a) cond.	39.5	6.91	9	23.1
<i>p</i> -iso-C ₄ H ₁₀ -Cl (b) cond.	39.5	6.75	9	22.7
<i>t</i> -iso-C ₄ H ₁₀ -Cl	39.5	6.93	81	18.7
<i>t</i> -iso-C ₄ H ₁₀ -Cl cond.	39.5	6.79	81	18.4
C(CH ₃) ₄ ^d	38.8	6.18	324	14.3
C(CH ₃) ₄ -Cl ^d	40.1	7.33	27	21.9
CF ₃ H	38.7	5.11	3	21.2
CF ₃ H-Cl	40.0	6.86	3	26.2
CCl ₃ H	40.1	6.88	3	26.2
CCl ₃ H-Cl	41.1	7.73	3	28.2

^a Units of ABC are [molecular weight $\times \text{\AA}^2$]³. ^b These values are $\log_{10} A$ where A is the moment of inertia.

^c "cond." stands for the condensed CH₃ approximation.

^d The molecule was treated as a series of spherical shells.

TABLE II
RELATIVE A FACTORS FOR CHLORINE ATOM REACTIONS
Cl + RH = HCl + R

Compounds		Relative A factors/H atom	
X	Y	Caled.	Exptl.
Hydrogen/methane		9.8	6.3 \pm 2
Methane/ethane		3.58	0.39 \pm 0.03
Ethane/neopentane		5.43	2.0 \pm 0.1
Ethane/chloroform		9.46
Ethane/fluoroform		2.08
<i>p</i> -Propane/ <i>sec</i> -propane (a)		0.89 ^a ; 0.82 ^b	0.61 \pm 0.05
<i>p</i> -Propane/ <i>sec</i> -propane (b)		0.87 ^a ; 0.87 ^b	
<i>p</i> -isobutane/ <i>t</i> -isobutane (a)		1.14 ^c	0.75 \pm 0.1
<i>p</i> -isobutane/ <i>t</i> -isobutane (b)		0.95 ^c	
		Relative A factors per molecule, ^c A_X/A_Y	
Ethane/propane ^c		1.9 ^a ; 1.6 ^b	0.68 \pm 0.04
Ethane/isobutane ^c		2.8 ^b	0.61 \pm 0.04

^a Calculated for the complete molecule. ^b Calculated using the condensed approximation. ^c These results are given in terms of the molecule as a whole because no experimental distinction was made between the different types of hydrogen atoms.

invite further work on other series of reactions which might likewise be compared with theoretical predictions.

The Calculations.—Values for the translational and rotational entropies have been calculated for each of the reactants and complexes studied. The translational entropies were calculated from the Sackur-Tetrode equation; the values are given in Table I. The values obtained for the rotational entropies depend upon the precise configurations assumed for the molecules (see below). These calculations of the moments of inertia can be considerably simplified if the hydrogen atoms of the methyl groups are "condensed" into the appropriate carbon atom; each methyl group is then treated as a mass of 15 located at the center of gravity of the original methyl group. Some examples of such condensations are given in Table I, and it can be seen from Table II that this simplification yields values of the relative A factors which are only slightly different from those obtained by more laborious means.

The Configurations.—It was assumed throughout that the carbon valency angles were all equal to 109.5°. In the linear C-H-Cl groups of the activated complexes the C-H distance was taken as 1.15 Å. and the H-Cl as 1.45 Å.; other bond lengths assumed were C-C 1.54 Å., C-H 0.98 Å., C-F 1.36 Å. and C-Cl 1.76 Å. The following points may be mentioned in connection with the configurations of individual reactants and complexes.

Propane.—Calculations were made for two different configurations of the complex obtained by attack of the chlorine atom at the primary position: (a) in which the chlorine atom in the complex is at the greatest possible distance from the third carbon atom (*i.e.*, with the C-H-Cl bond parallel to the opposite C-C bond) (b) in which the chlorine atom is as close as possible to the third carbon atom.

Isobutane.—Calculations were again made for two configurations of the complex: (a) in which the chlorine atom was at the greatest possible distance from the tertiary hydrogen atom (*i.e.*, the C-H-Cl bond parallel to the tertiary C-H bond); (b) in which the chlorine atom is as close as possible to the tertiary hydrogen atom.

Neopentane.—This molecule was treated as a central atom of mass 12 surrounded by two spherical shells one of mass 48 and radius 1.54 Å. and the other of mass 12 and radius 2.20 Å.; the chlorine atom in the complex was taken to be a distance of 3.65 Å. from the central carbon atom.

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The Crystal Structure of Nitramide, NH_2NO_2

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The structure of the unstable crystals of nitramide, NH_2NO_2 , has been investigated. The monoclinic unit cell has dimensions $a = 6.65$, $b = 4.79$, $c = 7.86$ Å, $\beta = 112^\circ 24'$, and the space group is $A2/a$. Good agreement ($R = 16\frac{1}{2}\%$) is obtained for all reflexions with one index zero and for all the planes with $k = 1$. The parameters chosen are N_I at $(0.250, 0.575, 0)$, N_{II} at $(0.250, 0.866, 0)$, O at $(0.367, 0.466, 0.137)$, whilst the probable hydrogen positions are $(0.42, 0, 0.08)$. The hydrogen atoms did not show up in the b -axis difference maps (although these showed evidence of anisotropic movements of the nitrogen and oxygen atoms) but there were indications of the hydrogen positions in the other two difference maps.

Introduction

The high melting point and low volatility of nitramide indicate a high degree of hydrogen bonding in the crystal. Because the compound contains a high proportion of hydrogen atoms to heavier atoms, it appeared that a study of the crystal structure might have provided interesting information on the N-H-O hydrogen bond. Furthermore, it was hoped that the study would throw light on the disputed question of the structure of the compound.

The chemical and physical properties of nitramide indicate (Bell & Trotman-Dickenson, 1949) that in solution it is predominantly in the form of NH_2NO_2 molecules, the structure originally suggested by Thiele & Lachmann (1895). However, a small proportion of the dissolved molecules probably have the tautomeric structure $\text{NH}.\text{NOOH}$ suggested by Pedersen (1934).

The present work indicates that the structure of the crystals is that shown in Fig. 1, and suggests that the formula NH_2NO_2 is to be preferred although it proved difficult to locate the hydrogen atoms precisely. All the presumed hydrogen bond distances are rather long, each amide nitrogen having six N-O distances of 3.1 Å.

Experimental details and unit cell

The nitramide was synthesized by the method of Marlies, LaMer & Greenspan (1939) (we are indebted to Mr J. S. Slater for this preparation). The nitramide was dissolved in anisole at about 25°C . to form a saturated solution. This was stored in a refrigerator (6°C .) at which temperature the crystals precipitated out. They were kept under these conditions for several months. When mounted on a goniometer head in the X-ray camera the crystals completely disappeared in 24 hours.

The crystals have the shape of laths of a few millimetres length and of width about 0.4 mm. and thickness 0.2 mm. Many were striated parallel to the long dimension. They show a parallel extinction. It was not easy to find good single crystals, but, when found, X-ray photographs showed them to be monoclinic, with the unique (b) axis parallel to the length. The dominant form was $\{101\}$ referred to the axes given below. The axial lengths were calculated from the position on the films of moderately high order spots. The cell found was:

$$a = 6.65 \pm 0.03, \quad b = 4.79 \pm 0.03, \quad c = 7.86 \pm 0.03 \text{ Å} \\ \beta = 112^\circ 24'.$$

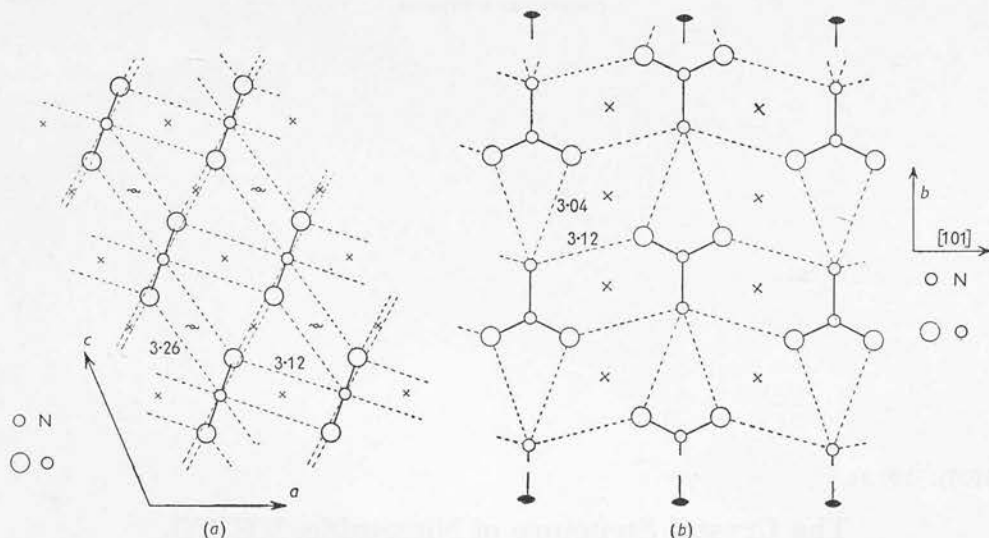


Fig. 1. (a) Projection of the structure down the b axis. The two nitrogen atoms are superimposed in the positions of the twofold axes. The broken lines show distances between the atoms of the different molecules. (b) One of the approximately flat sheets of molecules parallel to the $(10\bar{1})$ plane, the broken lines showing the bonding between molecules in the plane.

This cell contains 4 molecules of NH_2NO_2 , the observed density being 1.783 g.cm.^{-3} . The calculated density agrees with this to 1 part in 4000.

Photographs were obtained about the three principal axes. The b -axis films included Weissenberg photographs of zero and first layer lines, one being a multiple-film exposure of the zero layer line. The a -axis photographs were a number of oscillation photographs for adjustment purposes and a zero-layer-line Weissenberg exposure. About the c axis a set of oscillation photographs were obtained. Spots were visible on the photographs up to the limit of $\text{Cu } K\alpha$ radiation. The specimens used were chopped to a roughly cylindrical shape about the three axes, using a razor blade.

Space group and method of analysis

The a -axis zero-layer-line Weissenberg photograph showed that the $(0kl)$ spots are present only when $(k+l)$ is even. The b -axis photographs show that the $(h0l)$ spots are present only when h and l are both even, and that the $(h1l)$ spots are present only when l is odd. These absences are explained by the rules that (hkl) is present only when $k+l$ is even, and $(h0l)$ is present only when h is even. These rules suggest as space group either A/a or $A2/a$. The more symmetrical space group was chosen as it possesses the necessary number of general positions (eight) for the oxygen and hydrogen atoms and puts the nitrogens on to special positions. This situation provides a very simple problem, and as a satisfactory structure was reached on this assumption a detailed consideration of structures based on A/a was considered unnecessary.

The space group $A2/a$ contains centres of symmetry, rotation axes, screw axes and two kinds of glide plane

perpendicular to the b axis. The general equivalent points are

$$(0, 0, 0) \text{ and } (0, \frac{1}{2}, \frac{1}{2}), \pm(x, y, z), (\frac{1}{2}+x, \bar{y}, z).$$

The nitrogen atoms cannot be situated on the centres of symmetry, so that they must be placed on the rotation axes. Neglecting the hydrogen atoms for the time being, we are left with only one oxygen to find in the b -axis projection. This was done by means of the Patterson projection using the $(h0l)$ planes. This projection showed one 2N-O peak which gives the (x, z) coordinates of the oxygen with respect to the nitrogens. Assuming an N-O distance of 1.2 \AA we then obtained the y parameter difference between N and O , and assuming an N-N distance of 1.45 \AA we could also get the y parameter difference between the nitrogens. Then, from the $(0k0)$ intensities, we deduced the absolute values of the y coordinates of all the atoms. These were used to calculate the $(hk0)$ and $(0kl)$ intensities, and gave excellent agreement. Refinement was carried out by Fourier difference maps down all three axes.

On the b -axis difference map there were typical 'clover-leaf' patterns, suggesting some anisotropy of the heat motion of the two nitrogen atoms and also of the oxygen atom. This heat motion is a maximum in a direction roughly perpendicular to the plane of the molecule, i.e. perpendicular to $(10\bar{1})$. The hydrogen atom did not show up clearly on the b -axis projection, possibly owing to the heat-motion effects and to its being quite near the oxygen position, but the parameters given for the hydrogen atom are reasonable from the other two projections.

Table 1 shows calculated and observed F values for the $(h0l)$, $(0kl)$ and $(hk0)$ planes. The accuracy is

Table 1. Observed and calculated F values of nitramide

h	l	F_o	F_c	h	l	F_o	F_c	k	l	F_o	F_c
0	2	35	33	4	4	19	-29	4	0	0	-2.0
	4	8.5	-5.6	2	2	0	0.8	2	2	17	-14
	6	29	28	0	0	11	-10	4	4	22	-22
	8	29	26	2	2	29	-29	6	6	6.0	-4.4
2	10	24	-21	4	4	12	-12	5	1	0	-4.2
	8	22	-26	8	6	14	23	3	3	8.4	7.7
	6	1.7	0.8	4	4	4.8	2.4	5	5	0	3.4
	4	18	-13	2	2	5.2	4.8	6	0	0	-0.5
	2	73	-81					2	2	0	-5.0
	0	45	-41	k	l	F_o	F_c	h	k	F_o	F_c
	2	11	7	1	1	39	-38	1	2	21	15
	4	30	-25	3	3	30	29		4	0	1
	6	34	-31	5	5	5.2	7.2	6	6	0	2
	8	6.4	-6.4	7	7	19	-19	2	2	6.5	-10
4	10	21	22	9	9	0	-0.6	4	4	12	10
	8	4.7	3.2	2	0	55	45	3	2	7	5
	6	7.7	4.8	2	2	0	2.0	4	4	14	17
	4	37	45	4	4	19	-18	4	2	21	-17
	2	31	35	6	6	8	12	4	4	20	-20
	0	7.0	-5.6	8	8	12	14	5	2	7	-5
	2	20	18	3	1	22	-25	4	4	15	-18
	4	38	33	5	5	0	-1.8	6	2	0	1
	6	9	10	7	7	17	-18				
6	8	4.8	-2.4								
	6	27	-27								

highest for the ($h0l$) planes since the crystal habit is difficult for the other two projections. The ($hk0$) intensities are the least accurate of all, being derived only from oscillation photographs. The reliability index R is 16½% for all these planes. Intensity values were also calculated for the $k = 1$ planes and showed good agreement.

Description of the structure

The parameters finally chosen are:

	x	y	z
N_I	0.250	0.575	0
N_II	0.250	0.866	0
O	0.367	0.466	0.137

with a probable hydrogen position of (0.42, 0, 0.08). Fig. 1(a) shows a projection of the structure down the b axis, and gives the position of the nitrogen and oxygen atoms. The planar molecules are inclined at 6° to ($10\bar{1}$) and thus form almost flat layers parallel to this plane. One of these layers is shown in Fig. 1(b), and the remarkable number of N_II -O bonds is shown in this figure; each N_II is bonded to four oxygen atoms in the sheet, and each oxygen to two N_II atoms. Between different sheets the N_II -O distances are 3.28 and 3.5 Å, but there is one N_I -O distance of 3.12 Å. Probably this involves a van der Waals repulsion which is responsible for the departure of the molecules from the exact ($10\bar{1}$) plane.

The interatomic distances and angles found within the molecule are:

$$\begin{aligned}\text{N}_\text{I}-\text{N}_\text{II} &= 1.40, \quad \text{N}_\text{I}-\text{O} = 1.18, \quad \text{O}-\text{O} = 2.13 \text{ Å}, \\ \text{O}-\text{N}_\text{I}-\text{O} &= 129^\circ.\end{aligned}$$

These agree well with the dimensions of the nitro group obtained from other determinations, and the $\text{N}_\text{I}-\text{N}_\text{II}$ distance suggests that this bond is single.

Other interatomic distances are: within one sheet, between molecules separated by b :

$$\text{O}-\text{N}_\text{II} = 3.04 \text{ Å};$$

between molecules side by side:

$$\text{O}-\text{N}_\text{II} = 3.12 \text{ Å}.$$

The hydrogen atoms lie roughly between these two bonds. Between separate sheets are the following interatomic distances:

$$\text{O}-\text{N}_\text{II} = 3.26, \quad \text{O}-\text{N}_\text{II} = 3.50, \quad \text{O}-\text{N}_\text{I} = 3.12 \text{ Å}.$$

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RECENT DEVELOPMENTS OF GAS KINETICS

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The theoretical framework of gas kinetics has developed little since before the war, but much significant experimental work has been reported. This article outlines the most important developments in the study of the kinetics of homogeneous gas reactions which have taken place since 1945. Particular attention has been paid to elementary reactions whose study is now possible with the aid of novel techniques. It seems probable that development will continue along these lines.

CHEMICAL kinetics, the science of the rates of chemical reactions, is one of the two major branches of physical chemistry. Gas kinetics is that part of the subject which is concerned with the reactions of gases.

The most straightforward reason for kinetic investigations is the urge to find out by the measurement of rates, what happens in a particular reacting system. More specific reasons are to find the best conditions for a synthesis, to discover the mechanism of a reaction, or to determine the strength of a bond. The ultimate aim is to ascertain why reactions occur at the rate they do. This goal is still a long way off but gas reactions seem to offer the best path by which to reach it. Much is known of the motions of molecules in gases and there are few complications such as solvation and adsorption effects. Progress in the subject may therefore best be surveyed in relation to this goal.

The selection for discussion of the period since the 1939-45 war is partly a matter of convenience. Very little work was carried out during the war but there has been great activity in the field ever since. A crude analysis of the references from two books indicates the volume of work that has been published. Both books surveyed the state of knowledge at the time at which they were written. Of 2100 references in E. W. R. STEACIE'S comprehensive *Atomic and Free Radical Reactions*¹ 900 were published after the end of 1945; 450 out of 810 references in A. F. TROTMAN-DICKENSON'S *Gas Kinetics*² were published since 1945. Roughly equal numbers of papers have come from Canada, the United States and the United Kingdom and very few from other countries.

ELEMENTARY REACTIONS

The majority of the systems that are investigated by the worker in gas kinetics are now known to be chemically complex. That is, the final products are not formed by a single reaction but are the overall result of a series of elementary reactions. These elementary reactions are so called because they are believed to occur exactly as indicated by the appro-

priate chemical equation. No series of constituent reactions need be postulated to describe them. This insistence on the fundamental importance of elementary reactions has been a distinguishing feature of work in gas kinetics since the war. Before the war reasonably successful attempts were made to explain many overall chemical changes which were observed in terms of elementary reactions. The recognition of the importance of chain reactions consisting of the repetition of the same simple elementary reactions was a major achievement. At present much research is deliberately planned to yield information on specific elementary reactions.

This work is now possible because of technical advances, particularly in analysis. The most generally useful analytical tools have been the low temperature still, the mass-spectrometer and, to a lesser extent, the infra-red spectrometer. These devices were perfected during the war by workers in oil companies, being required for analytical control in the production of high octane petrol.

If an elementary reaction involves one molecule it is said to be unimolecular and its rate constant, k , is expressed in sec^{-1} . The rate constant of a bimolecular reaction is expressed in $\text{mole}^{-1} \text{cm}^3 \text{sec}^{-1}$, and the rate constants of the comparatively few termolecular reactions are expressed in $\text{mole}^{-2} (\text{cm}^3)^2 \text{sec}^{-1}$. The variation of the rate constant of a reaction with temperature may be expressed by the equation

$$k = A \exp(-E/RT)$$

where R is the gas constant and T the absolute temperature. A is known as the A factor, E as the activation energy, and A and E together are known as the rate factors of the reaction. All theoretical calculations of k involve the separate consideration of A and E .

TRANSITION STATE THEORY

H. EYRING, M. POLANYI and their co-workers developed the transition state theory of chemical reactions in the years immediately preceding the war. This theory is the most generally successful that has

yet appeared. It postulates that reactants must pass through a definable critical state of high energy (the transition state or activated complex) before they become products (see Figure 1). It then states that:

$$A = \frac{RT}{Nh} \exp (\Delta S^\ddagger / R) \approx 10^{13} \exp (\Delta S^\ddagger / R)$$

where N is Avogadro's number and h is Planck's constant. The entropy of activation, ΔS^\ddagger , is the difference between the entropy of the activated complex and that of the reactants. The accuracy of the calculation of these entropies is dependent upon the information available about the physical

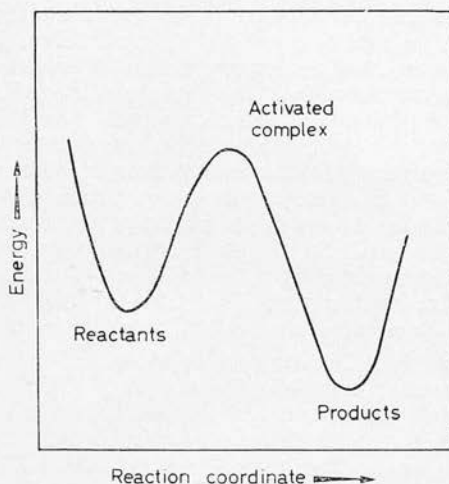


Figure 1

properties of the reactants and the complex. There is always some uncertainty as to the precise configuration of the complex but this rarely causes an uncertainty in A greater than a factor of 10.

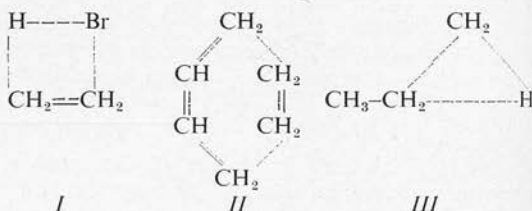
In principle the activation energy may be calculated by quantum mechanics but the calculation is prohibitively involved. Eyring and Polanyi showed that E was generally of a magnitude which was consistent with the knowledge of potential energy curves derived from spectroscopy. This has been a great aid to understanding.

Most elementary gas reactions may be classified under one of three headings:

- (1) Decomposition-combination $AB = A + B$
 - (2) Transfer $A + BC = AB + C$
 - (3) Addition to double bonds—the decomposition of radicals $A + B = C = A - B - C$
- Free radicals are involved in all except the first class of reaction.

D. H. R. BARTON, A. MACCOLL, and their collaborators have studied, in the past ten years, the

thermal decomposition of many alkyl chlorides and bromides. The rates of the reactions were found to depend markedly upon the structure of the alkyl groups. The decompositions do not involve free radicals, for the products result from the rearrangement of four-membered cyclic transition states of type I.



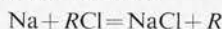
The halides are not unique in decomposing in this way, the decompositions of many other compounds are similar but they have not been so systematically investigated. Cyclic transition states (with 6 members) are also involved in Diels-Alder reactions, as is shown for ethylene and butadiene (II). Evidence is now accumulating that the addition of methylene biradicals to paraffins involves a transition state with only three members (III). No satisfactory explanation has yet been advanced for the great variations in the rates of decomposition of the different alkyl halides.

The other important class of decompositions includes those reactions in which an atom or radical splits off from a normal molecule. Hardly any of these reactions were accurately studied before the 1939-45 war, though it was shown that according to the transition state theory the activation energy of the decomposition should be approximately equal to the strength of the bond broken. Great interest attaches to the strengths of bonds. First, they are quantities which one would expect a satisfactory theory of valence to predict. Second, they are needed for the interpretation of the energetics of radical reactions. The recent experimental studies have largely been made possible through the development of flow techniques, by M. SZWARC following Polanyi, particularly with the use of toluene as a carrier gas to trap the reactive radicals. There appear to be many reactions, such as the decomposition of ethyl benzene into methyl and benzyl, for which the activation energy is equal to the bond strength. In these cases A is usually equal to $10^{13 \pm 1.5} \text{ sec.}^{-1}$ which is the expected magnitude for a reaction in which the configuration of the transition state is thought to be very similar to that of the initial state. Several reactions are known, however, that either have an A factor greater than $10^{14.5} \text{ sec.}^{-1}$ or an activation energy greater than the

accepted bond strength or both. Sometimes the large A factor may be plausibly ascribed to a large increase in entropy in passing from the initial to the transition state, as may occur when ethane approaches the state of two freely rotating methyl groups. This explanation does not always account satisfactorily for the high values of A and it throws no light on the problem of the high values of the activation energy.

Very few rate constants of combination reactions have been measured because of the difficulty of determining the concentrations of radicals which are usually of the order of 10^{-10} mole cm^3 . The few reactions of simple radicals which have been investigated all appear to have rate constants of about $10^{13.5}$ mole $^{-1}$ cm^3 sec $^{-1}$ and very low activation energies.

Most of the reactions in the second group which have been investigated involve the transfer of a hydrogen atom, though Polanyi measured the rates of many reactions of the type



before 1939 and the work has since been extended. The investigator has to solve three problems before the rate constant of a transfer reaction can be measured. It is necessary to find a suitable source of atoms or radicals, to devise methods of determining their concentrations and to measure the rates of formation of the significant products. Hitherto photolytic sources of radicals have proved most convenient because of the ease with which they are controlled. The other problems have been successfully solved for systems involving chlorine atoms, methyl radicals, trifluoromethyl radicals and ethyl radicals, though extensive work has only been carried out on the first three. Some typical results are presented in Table 1.

There are a number of features which call for comment. First, the A factors are of the order predicted by the transition state theors. Second, the activation energies are very much lower than the strengths of the bonds broken; this can also be understood in terms of the theory. Third, the general trend towards lower activation energies as the bonds get weaker is expected. However, the interpretation of the results on these simple reactions still presents many problems. In particular, the polar nature of the transition states is evidently important but no quantitative treatment has been proposed.

The third group of reactions has been much less fully investigated, although the addition of radicals to unsaturated compounds is the same reaction as the chain carrying steps in liquid phase polymerizations

whose rates have been much measured. This is not because the reactions are of little theoretical interest, but because of the difficulties inherent in their study. The decompositions of radicals containing three or more carbon atoms are difficult to study because suitable sources of free radicals have not been

Table 1. The Rate factors of the reactions $X + \text{RH} = \text{XH} + \text{R}$

R	X			D(R-H)
	Cl	CH ₃	CF ₃	
H (a)	13.9	11.5	11.6	104
(e)	5.5	11.1	8.8	
CH ₃ (a)	13.4	11.2	11.8	103
(e)	3.9	12.8	10.3	
C ₂ H ₅ (a)	14.1	11.3	11.7	98
(e)	1.0	10.4	7.5	
sec-C ₄ H ₉ (a)	14.3	11.0	11.2	94
(e)	0.7	8.3	5.1	
tert-C ₄ H ₉ (a)	14.3	10.9	11.2	90
(e)	0.9	7.5	4.7	
neo-C ₅ H ₁₁ (a)	14.1	11.3	11.8	98
(e)	0.7	10.2	7.6	
References	3, 4	1, 2	5, 6, 7, 8	1, 2

(a) is $\log A$ in mole $^{-1}$ cm^3 sec $^{-1}$, (e) is E in kcal mole $^{-1}$, $D(\text{R-H})$ is the strength of the RH bond in kcal mole $^{-1}$

developed. Photolyses which have been so useful as sources of smaller radicals are not generally satisfactory. When a large molecule is photolysed it rarely splits simply into the required radicals. The analytical problems to be solved are, therefore, formidable. Consequently the interpretation of the necessarily incomplete information is uncertain. Similar analytical difficulties have beset the study of the addition of small free radicals to unsaturated compounds. Nevertheless Steacie and his collaborators have obtained evidence that the activation energies of these reactions are low. The A factors are about 10^{11} mole $^{-1}$ cm^3 sec $^{-1}$, which is the expected order of magnitude. Unfortunately these results seem to be in conflict with the scanty data on the complementary decompositions.

The rates of these decompositions and those in the first group of reactions may depend upon the rate at which energy is transferred between molecules at low pressures. The effect occurs because, although the decompositions only involve one molecule, that molecule can only acquire the energy necessary for reaction by collision with other molecules. The first satisfactory theoretical treatment of this behaviour

was given by F. A. LINDEMANN and C. N. HINSHELWOOD in the twenties. For several years much attention was paid to the verification of the original theories and the various extensions and improvements. However, in the period immediately preceding the war, little work was done on the topic. After the war, interest revived, first because it was felt that the original experimental work was not satisfactory, and second because some problems of high speed flight involved a knowledge of energy transfer. Consequently much of the original work has been re-examined using modern methods. Furthermore, new direct techniques involving the electronic recording of transient phenomena have been developed for following very rapid reactions. As a result of these two approaches a fairly satisfactory picture of the factors which determine the rate at which energy is transferred between molecules is beginning to emerge. Generally the early theories have survived the test very well.

OXIDATION AND COMBUSTION

One major field of research in gas kinetics remains to be considered. It is that of oxidation and combustion. All homogeneous reaction systems involving oxygen are very complex, furthermore, it is often difficult to eliminate complicating heterogeneous effects. As a result, the study of oxidations is still in a primitive stage despite the importance of the subject and the immense amount of work which has been devoted to it. During the thirties Hinshelwood and N. SEMENOV successfully accounted for the form of the experimental results in terms of special types of branched chain reactions. Since the war many attempts have been made to determine the nature of the elementary reactions which make up the chains. No reaction scheme has yet been generally accepted. It seems possible that further advances will be made by isolating some of the likely elementary reactions for study in systems which do not contain molecular oxygen. This is the procedure which has proved successful in the elucidation of the simpler, but analogous, chain decompositions of organic compounds.

POSSIBLE FUTURE DEVELOPMENTS

No theoretical advances of the first importance have been made in the last ten years. Work during this period has resulted in the notable accumulation of many reliable measurements of rates. It seems that this pattern of development will continue. The outstanding theoretical need is for a method of calculating activation energies. Enough is now known of this problem in quantum mechanics for the difficulty of solving it to be realized. On the other hand, the prospect of more and better determinations

of significant rate constants is excellent. Electronic methods are being increasingly used to study reactions that are complete in a fraction of a second and are too fast to be followed by simpler techniques. R. G. W. NORRISH and G. PORTER have developed flash photolysis whereby sufficiently high radical concentrations to permit direct measurement may be momentarily generated. Another method of measuring the concentrations of free radicals which will certainly be further exploited depends upon the direct attachment of a reactor to the ionization chamber of a mass-spectrometer. Increasing attention is being paid to the unexplored class of reactions which occur at the very high temperatures that can be generated by shock waves. The study of the reactions of molecules that have been raised to a known electronic or vibrational state is just beginning; these states correspond to immensely high ambient temperatures. Much of the preliminary work has been done in Russia. The molecules are often excited by the absorption of light; if the light is monochromatic, all the excited molecules will be in the same known electronic and vibrational state. However, none of these approaches is likely to yield such important results as the further development of conventional investigations through the use of gas chromatography. This method of analysis has been described recently by one of its originators A. T. JAMES⁹. It is now a simple matter to analyse the products of a complex reaction system very completely. Hitherto such analyses could only be performed with very costly equipment. Moreover, they took so long that no one would attempt the many repetitions needed to establish a rate constant. During the next few years it should be possible, with gas chromatography, to investigate thoroughly the reactions of radicals containing more than three carbon atoms and the transfer of atoms other than hydrogen.

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THE TEACHING OF CHEMICAL KINETICS

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Nor long ago I agreed to talk to a school science society on recent developments in chemical kinetics, especially on those connected with free radicals. One of the difficulties was to decide what knowledge I could assume the audience to possess. To obtain information on this point I read the chapters on kinetics in some eight or ten widely-used school texts on physical chemistry. The experience was rather shattering, for these chapters contained a very large number of errors, many of them common to several books. As far as I could judge, the chapters on kinetics were unique in this respect, for the rest of the books were, when allowing for the necessary simplifications, substantially correct and up-to-date. The probable cause of the trouble is the lack of any modern, conveniently available text on kinetics, on which the authors could rely. Accordingly, it seemed that a few suggestions might be helpful.

An almost universal error is the failure to distinguish clearly (or at all) between order and molecularity. Modern practice which is universally accepted among workers in the field is straightforward and could well be adopted in schools: it may be briefly stated. The order of a chemical reaction describes the mathematical form in which the experimental observations are best cast. Thus a first order reaction involving the formation or disappearance of a substance "M" can be described in terms of one concentration variable. For instance the reaction:



is said to be first order if:

$$-\frac{d[A]}{dt} \equiv -\frac{d[B]}{dt} \equiv \frac{d[X]}{dt} \equiv \frac{d[Y]}{dt} = k[A] \text{ or } k'[B]$$

where $[M]$ represents the concentration of the species M. If the value of k or k' is dependent upon the concentration of some substance whose concentration does not effectively change during the course of the reaction, the behaviour is sometimes described as pseudo-first order. Many examples of this are to be found in the literature of acid-base catalysis. This usage

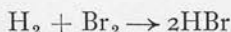
is best avoided as it is liable to lead to confusion ; if equation (1) is satisfied by the experimental observations, the reaction should be described as first order.

Similarly a reaction is described as being second order if the experimental results best fit a relation of the type :

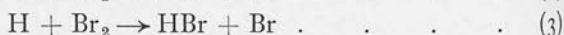
$$-\frac{d[A]}{dt} \equiv -\frac{d[B]}{dt} \equiv \frac{d[X]}{dt} \equiv \frac{d[Y]}{dt} = k[A][B]$$

The definition of third and fourth order reactions is exactly parallel. It may be noted, though probably no one will want to teach this at school, that reactions of fractional order are possible, and do in fact occur, as in the thermal para- to ortho-hydrogen conversion or the decomposition of ozone catalysed by nitrogen pentoxide.

From what has been said it is clear that the order of a reaction does not necessarily describe the *mechanism* by which the reaction takes place. During the last twenty years emphasis has increasingly been laid upon the study of the elementary chemical reactions which go to make up the overall chemical process that is normally observed. Thus the thermal combination of hydrogen and bromine which may be represented by the stoichiometric equation :



is known to take place by the mechanism :



Each of these individual steps is called an elementary reaction, by analogy with the definition of an element, because it cannot be split up into a series of simpler chemical processes. Incidentally this is a good example of the limitations of the concept of the order of a chemical reaction, for the rate of formation of hydrogen bromide is given by the expression :

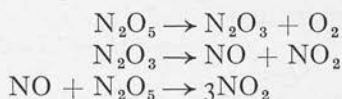
$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + m \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

obviously no simple order can be assigned to this process.

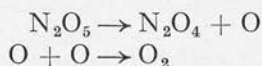
Each of the reactions (1), (2), (3) and (4) is an elementary reaction. Each of the reactions (2), (3), (4) is a bimolecular reaction because each only involves two molecules. The two molecules would have a finite probability of reaction if they alone were enclosed in a box. Similarly a unimolecular reaction is one in which the chemical change of a molecule can take place in the absence of all other molecules (the question of energy transfer is irrelevant for the present purpose). The connection between the idea of an elementary reaction and the idea of molecularity can thus

be seen. If an elementary reaction can be isolated, its order and molecularity will be the same. It is only correct to talk about the molecularity of an elementary process, therefore the use of the term molecularity implies a knowledge or assumption of the mechanism of the reaction. To recapitulate, to say that a reaction is unimolecular means that one specified molecule alone takes part in the reaction, bimolecular means that only two specified molecules take part in the reaction, termolecular three, tetramolecular four, etc., in each case it is implied that the reaction is thought to be elementary. The order of a reaction merely describes the experimental findings, the molecularity postulates a mechanism which may subsequently be shown to be incorrect.

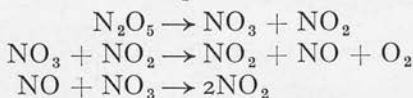
The second point I have to make concerns the examples which are almost universally quoted of reactions of different order and molecularity, especially the examples of gas reactions. The examples are often not well chosen, for the reactions considered are usually known to be much more complicated than the authors imply and are unsuitable for presentation in schools. The decomposition of nitrogen pentoxide is frequently quoted as an example of a unimolecular [*sic*] reaction. Sometimes the mechanism associated with Daniels is given, namely:



Mee (1951) gives as an alternative a mechanism apparently contrived by himself:



Now a proposed mechanism of a reaction can never be shown to be correct, at most it can be shown that no simpler mechanism would fit the experimental facts, but it is quite possible to prove that a mechanism is incorrect. The second mechanism is obviously incorrect, for the first step is known from measurements of heats of formation to be about 56 Kcal. endothermic while the overall activation energy of the decomposition is only 24.7 Kcal. The first mechanism was proved to be incorrect by Ogg (1947), who proposed the mechanism which is now accepted:



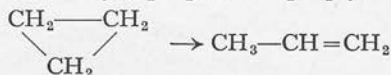
However, the reaction is quite unsuitable for presentation to school children unless the teacher is prepared to describe the use of radioactive tracers, the effect of isotopic substitution on the vibrational spectra of molecules, the use of the cathode ray oscillograph in the study of chemical reactions, etc. It takes one hour to deal with the reaction when lecturing to third-year undergraduates taking Honours Chemistry.

The other examples which I have found quoted as unimolecular reactions include the pyrolyses of acetone, acetaldehyde, propionaldehyde, dimethyl ether, diethyl ether, azomethane, azoisopropane and sulphuryl chloride and the racemization [*sic*] of pinene. All these reactions except the last are known to occur at least in part by free radical chain mechanisms which have not yet been completely elucidated. Only in a few cases have the products of the reactions been analysed so that it is not known whether a simple stoichiometric equation for the reaction can be written or not. The products of the azomethane decomposition are certainly complicated.

The isomerization of pinene is probably a homogeneous unimolecular reaction but it is an unfamiliar compound which seems to react by a rather unusual intramolecular process (Burwell, 1951). For these reasons none of the reactions is really suitable for didactic purposes.

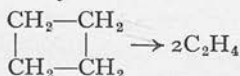
This looks bleak. However, there are a number of homogeneous unimolecular gas reactions which occur cleanly and which have been fully investigated. Unfortunately they are not well adapted for classroom demonstration, but at least do involve fairly simple molecules and might well be introduced into elementary texts.

- (1) The isomerization of cyclopropane to propylene:



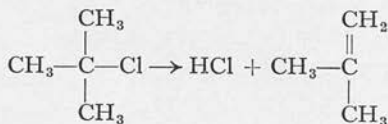
occurs at a convenient rate at about 490°C . It is followed by analysis for the propylene formed either by selective oxidation with potassium permanganate, selective hydrogenation on a nickel catalyst or by absorption of the olefin by mercuric acetate.

- (2) The decomposition of cyclobutane to ethylene:



occurs at a convenient rate at 450°C . It is followed either by the pressure change or by analysis for the ethylene by absorption with mercuric acetate. A similar reaction of perfluorocyclobutane is also known.

- (3) The decomposition of *t*-butyl chloride to isobutene and hydrogen chloride:



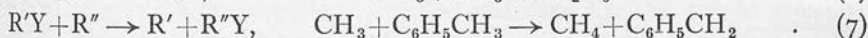
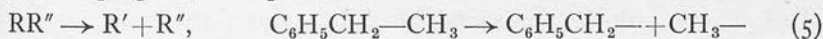
occurs at a convenient rate at 300°C . and may be followed by the pressure change or by analysis for the hydrogen chloride. The decomposition of *t*-butyl bromide at 250°C . is exactly similar.

There are comparatively few gas phase reactions involving ordinary molecules which are good examples of bimolecularity. The outstanding examples are still the decomposition of hydrogen iodide and the combination

of hydrogen and iodine. Another example is the synthesis of perfluorocyclobutane from tetrafluorethylene. The decomposition of nitrous oxide which is sometimes quoted as an example of a bimolecular reaction seems more likely to be a unimolecular reaction, whose rate is controlled by the process of energy transfer at normal pressures.

The first order reactions in solution which are usually cited, such as the rearrangement of *N*-chloracetanilide, the inversion of sucrose, the mutarotation of glucose and the hydrolyses of esters are none of them unimolecular. In fact, there are very few unimolecular reactions in solution. All the above reactions have disadvantages from the point of view of the teacher, even as examples of first order reactions, compared with the gas reactions, because if a more thoughtful pupil enquires how the reaction actually occurs, the teacher will have to embark on a lengthy explanation of a complex process.

Finally I should like to suggest that teachers might consider the advantages of free radical reactions as object lessons in kinetics. These reactions are formally very simple and the pupil should be able to visualize the process immediately. This is not so for, say, the rearrangement of *N*-chloracetanilide. There are three types of free radical reaction which are useful for the present purpose, examples of these are:



It can be seen that a reaction of type (6) is formally the reverse of a reaction of type (5) and in practice it is frequently profitable to consider the equilibria formed by such pairs of reactions.

Reaction (5) is a unimolecular, homogeneous reaction and has been investigated at temperatures around 600° C. Large numbers of this type of reaction are known and have been accurately studied, a short list of these is given in Table I. An excellent review of this type of reaction has been written by M. Szwarc (1950) who was personally responsible for many of the investigations. The frequency factors and activation energies calculated from the Arrhenius equation

$$k = Ae^{-E/RT}$$

for these reactions and also for those mentioned previously are given in the table.

These free radical reactions may very well be used as illustrations if the concept of activation energy is to be introduced to the pupils, for both the activation energies and frequency factors can be given simple physical meanings. The activation energy in these reactions corresponds to the strength of the bond broken, that is to the heat of the reaction. The simple qualitative generalization follows that the stronger the bond is, the higher the activation energy will be and the higher the temperature will be to which the compound must be heated before it will decompose at a given rate.

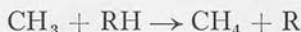
All the frequency factors of the free radical reactions in Table I are about $10^{13} \text{ sec.}^{-1}$, which is of the order of the stretching frequency of a single bond. It will be realized that after the required amount of energy to break a bond has been concentrated in the bond a certain time will elapse before the bond is stretched to such a length that it may be said to be broken. We may imagine two balls on a spring vibrating when suddenly sufficient energy is released in the system to break the spring. If at this moment the balls are just starting to move together, a complete vibration period will elapse before the spring breaks. The energy may be introduced at any moment during the vibration period so that the average life of the system after the energy has been introduced will be half the period of vibration. This, of course, is over-simplified but the most detailed theory predicts that the frequency factor A should be equal to the weighted root mean square frequency of all the vibrational frequencies in the molecule. There are special reasons why two of the decompositions to ordinary saturated molecules should have rather high frequency factors.

The rates of very few bimolecular reactions of type (6) have been measured because of the considerable experimental difficulties. However, it has been found that the rate constant for the combination of methyl radicals and ethyl radicals with their own kind are of the order of $10^{14} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$. Rate constants of this magnitude correspond to the combination on every collision of two radicals with kinetic-theory collision cross-sections, hence we may conclude that these reactions have no activation energy. This conclusion is supported by measurements of temperature coefficients. It is entirely plausible that the combination of two radicals each having a free valence should involve no barrier because they "fit" each other. Reactions of this type might serve in the introduction of students to the collision theory of chemical kinetics despite some obvious disadvantages.

The third type of reaction (7) may well be used to illustrate the important case of bimolecular reactions to which there is an energy barrier. Unfortunately the interpretation of reactions of this type is not straightforward, but some useful generalizations may be made. In Table II it can be seen that the A factor in the Arrhenius equation for the reaction of atoms with molecules approaches the collision frequency for molecules with kinetic-theory collision diameters (approximately $4 \times 10^{14} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$). Thus more support is found for the simple collision theory. The reactions of the more complicated radicals have lower frequency factors. It is plausible and not entirely misleading to ascribe this lowering to the need for more precise orientation of the molecules in collision in these cases. This idea of orientation is an over-simplification but it is hardly feasible to introduce the more accurate concept of entropy.

It is interesting to note that the activation energies for the attack of methyl radicals on the alkanes are monotonously graded, passing, from methane, to compounds containing primary hydrogen atoms only, to those

containing secondary hydrogen atoms, to those containing tertiary hydrogen atoms. This behaviour is observed in the attack of other radicals and atoms. The strengths of the relevant C—H bonds in some of these compounds are known and provide support for the reasonable conclusion that for a series of very similar compounds the activation energies of reactions of the type



will be lower the weaker are the R—H bonds. This rule must be applied with great caution as it is not universally applicable.

These free radical reactions may all be understood in terms of some simple generalizations which are admittedly over-simplified but are based on a solid foundation of truth. If the attention is concentrated entirely upon reactions involving ordinary saturated molecules it is impossible to convey any simple ideas on the important subject of why different chemical reactions take place at different velocities.

TABLE I
UNIMOLECULAR DECOMPOSITIONS

REACTION.	E Kcal./Mole.	$\log_{10} A$ sec. ⁻¹
Cyclopropane \rightarrow Propylene	65.0	15.17
Cyclobutane \rightarrow 2C ₂ H ₄	62.8	15.71
<i>i</i> -C ₄ H ₉ Cl \rightarrow HCl + <i>i</i> -C ₄ H ₈	41.4	12.4
<i>t</i> -C ₄ H ₉ Br \rightarrow HBr + <i>i</i> -C ₄ H ₈	40.5	13.3
$\phi\text{CH}_3 \rightarrow \phi\text{CH}_2 + \text{H}$	77	13.3
$\phi\text{CH}_2\text{Br} \rightarrow \phi\text{CH}_2 + \text{Br}$	51	13.0
$\phi\text{C}_2\text{H}_5 \rightarrow \phi\text{CH}_2 + \text{CH}_3$	63	13.0
$\phi\text{CH}_2\text{NH}_2 \rightarrow \phi\text{CH}_2 + \text{NH}_2$	59	12.8

TABLE II
BIMOLECULAR ATOM TRANSFER REACTIONS

REACTION.	E Kcal./Mole.	A mole ⁻¹ c.c. sec. ⁻¹ .
Br + H ₂ \rightarrow H + HBr	17.5	7×10^{13}
Br + CH ₄ \rightarrow CH ₃ + HBr	18.3	4×10^{13}
Br + CH ₃ Br \rightarrow CH ₂ Br + HBr	16.1	3×10^{13}
Na + C ₂ H ₅ Cl \rightarrow NaCl + C ₂ H ₅	10.2	5×10^{14}
CH ₃ + CH ₄ \rightarrow CH ₄ + CH ₃	12.8	—
CH ₃ + C ₂ H ₂ \rightarrow CH ₄ + C ₂ H ₅	10.4	1.9×10^{11}
CH ₃ + <i>n</i> -C ₄ H ₁₀ \rightarrow CH ₄ + C ₄ H ₉	8.3	2.2×10^{11}
CH ₃ + <i>i</i> -C ₄ H ₁₀ \rightarrow CH ₄ + C ₄ H ₉	7.6	2.0×10^{11}

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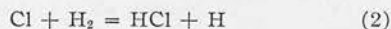
A METHOD FOR THE STUDY OF CHLORINE ATOM REACTIONS. THE REACTION $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$

Sir:

The reactions of chlorine with hydrogen and the hydrocarbons are chain reactions and as such their over-all rates are extraordinarily sensitive to the presence of traces of impurities, the condition of the reaction vessel and the intensity of the absorbed light in photochemical systems. Consequently, the many attempts which have been made to determine the rate constants of the elementary reactions of chlorine atoms, particularly those of type 1, have met with disproportionately little success.



However, the rate constant of the reaction 2 is known¹ to be given by $k_2 = 10^{13.9} \exp. (-5500 \pm 200/RT)$ moles⁻¹ cc. sec.⁻¹. So that if the rate of



reaction 2 can be compared with that of reaction 1 in the same reaction system, k_1 may be found without having to make a direct estimate of chlorine atom concentrations: we have done this and determined k_1 for the reaction with methane in the following way.

Measured quantities of methane and hydrogen were sealed up in a 160 cc. Pyrex reaction vessel together with some 2.55×10^{-4} mole of chlorine, which is frozen out. The reaction is started by placing the vessel in a liquid or vapor bath which raises its temperature very rapidly. After a short interval to allow the vessel to attain the desired temperature, it is strongly illuminated. When a convenient period has elapsed the vessel is re-attached to a vacuum system and the residual hydrogen and methane separated from the products by low temperature distillations and adsorption in silica gel and measured.

The available evidence indicates that the hydrogen atoms and radicals formed will react with chlorine molecules for these reactions probably take place on every collision and hence the rate constants are approximately one hundred times those of any competing process, so that reactions 1 and 2 are the only ones by which methane and hydrogen are removed or formed. Then it can be readily shown² that if

$-d[\text{CH}_4]/dt = k_1[\text{CH}_4][\text{Cl}]$ and $-d[\text{H}_2]/dt = k_2[\text{H}_2][\text{Cl}]$ then

$$k_1/k_2 = \log \{ [\text{CH}_4]_i / [\text{CH}_4]_f \} / \log \{ [\text{H}_2]_i / [\text{H}_2]_f \}$$

where the subscripts refer to the initial and final concentrations of the reactants. The reproducibility of k_1/k_2 for various ratios of methane to hydrogen is shown in the table. In Fig. 1 the logarithm of k_1/k_2 is plotted against $10^3/T$. The curvature of the points which is very small for a temperature range from 0° to 215° may be partially due to the effective temperature of the reaction being slightly below that of the bath at the

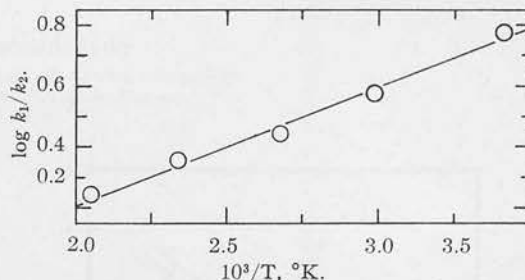


Fig. 1.

higher temperatures. However, it seems that this can cause only a very small error in the slope of the line. It can be seen that the variation of k_1/k_2 with temperature is given by $k_1/k_2 = 10^{0.59} \exp (-1700/RT)$. Hence $k_1 = 10^{14.5} \exp (-3800/RT)$ mole⁻¹ cc. sec.⁻¹.

RUNS AT 100°

Initial concn., 10^{-7} mole cc. ⁻¹		Amount reacted, 10^{-7} mole cc. ⁻¹		
$[\text{H}_2]$	$[\text{CH}_4]$	$\Delta[\text{H}_2]$	$\Delta[\text{CH}_4]$	k_1/k_2
28.34	27.96	2.22	6.96	2.76
35.98	44.81	2.75	8.98	2.81
58.15	52.19	4.72	7.54	3.01
66.57	33.80	5.27	6.46	2.57
76.77	33.27	5.24	7.72	2.88
81.34	51.16	4.09	8.62	2.79

Assuming that the standard entropy of the methyl radical is 45.5 e.u. and that the strength of the $\text{CH}_3\text{-H}$ bond is 102.5 kcal./mole at 25°, we can make use of the approximate relation $k = \exp (\Delta S^\circ/R) \exp (-\Delta H^\circ/RT)$ which neglects the small variations of ΔS and ΔH with temperature. Then we find for the equilibrium constant of reaction 1

$$K_1 = 10 \exp (1000/RT)$$

Therefore the rate constant, k_{-1} , of the reverse reaction is $k_{-1} = 10^{13.5} \exp (-4800/RT)$ mole⁻¹ cc. sec.⁻¹ which is equal to $10^{11.0}$ mole⁻¹ cc. sec.⁻¹ at 150°. At this temperature Cvetanović and Steacie³ find $k_{-1} = 10^{10.4}$ mole⁻¹ cc. sec.⁻¹; although they report an activation energy of only 2.3 kcal./mole for reaction (-1). However, their activation energy is based on points at 25° and 150° only and it is known that the study of the reactions of methyl radicals derived from the photolysis of acetone at low temperatures tends to yield low values for the activation energies.⁴

With slight modifications this method can be adapted to the study of many other chlorine atom reactions. The results will be reported in full when the program of work is complete.

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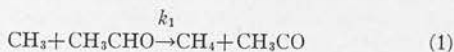
The Photolysis of Acetaldehyde

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(Received January 5, 1953)

THE high temperature photolysis of acetaldehyde using the rotating sector technique has been studied by Dodd.¹ From a consideration of his results and those of other workers, he concluded that all the available data led to $10^{12.8 \pm 0.47} \times \exp[(-10.7 \pm 0.5)/RT]$ for the rate constant of the chain-propagating step, where the units are mole, cc, and sec. However it seemed² that, in view of the relative rates of formation of methane and ethane in the low temperature photolysis, all high values for the activation energy of the reaction of methyl with acetaldehyde (generally believed to be the rate determining propagation step) should be viewed with suspicion, because the pre-exponential factor would have to be 10^9 greater than had ever been found for a methyl radical reaction of that type.

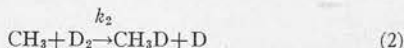
Recently the rate constant of the reaction



has been found by Volman and Brinton³ to be $4.2 \times 10^{10} T^{\frac{1}{2}} \times \exp[(7.5 \pm 0.3)/RT]$ from studies of the decomposition of di-*t*-butyl peroxide in the presence of acetaldehyde, combined with the value for the rate constant for the recombination of methyl radicals found by Gomer and Kistiakowsky,⁴ on which all rate constants referred to hereinafter are based.

We have recalculated the data reported by Danby, Buchanan, and Henderson⁵ on the amounts of methane and ethane formed in the photolysis of acetaldehyde at 300°C and find that $k_1 = 1.22 \times 10^9$.

Additional values of k_1 may be obtained by combining Majury and Steacie's⁶ value of $k_2 = 9.4 \times 10^{11} \exp(11.8/RT)$,

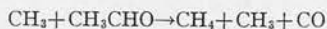


with Davison and Burton's⁷ values for k_1/k_2 at different temperatures.

A considerably less accurate point may be deduced making certain plausible assumptions from the work of Blacet and Brinton⁸ which seems to be the only data on the production of methane and ethane at low temperatures.

All these data, which have not been correlated before, are shown in Fig. 1. Bearing in mind the separate pieces of work upon which the values depend, the consistency is very satisfactory. This shows first that the older photolytic data cannot be interpreted as simply as had been supposed, and secondly, that the values of k_2 obtained by Davison and Burton using acetaldehyde as a radical source are in effective agreement with those of Steacie.

The most likely cause of the discrepancy between the value of E_1 and the temperature coefficient of the chain propagation in the photolysis is that the chain step cannot be written



but must be split into reactions (1) and (3)

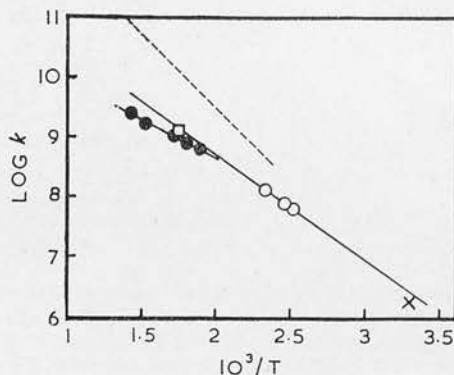
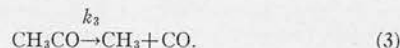
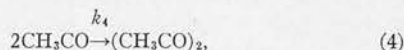


FIG. 1. Arrhenius plot for the reaction of methyl radicals with acetaldehyde. --- Dodd; ○ Volman and Brinton; □ Danby, Buchanan, and Henderson; × Blacet and Brinton; ● Davison and Burton.



This distinction will only be important if $k_1[\text{CH}_3\text{CHO}]$ is of the same order of magnitude as k_3 . Assuming as a maximum value that $k_1 = 5 \times 10^{13}$,



we may estimate from the work of Howland and Noyes⁹ a maximum value for k_3 at 25°C of 4 sec⁻¹ which may be compared with $k_1[\text{CH}_3\text{CHO}] = 10$ sec⁻¹ at the same temperature and 100-mm acetaldehyde pressure. Since E_3 is probably low, this near equality may persist over a considerable range of temperature. Furthermore, the kinetics deduced from the two assumptions may be almost indistinguishable if the rate equation for the decomposition should be written as $k_3'[\text{CH}_3\text{CO}]P$ where P is the total pressure of the system. This is very likely in view of the simplicity of the acetyl radical¹⁰ and the low value of E_3/RT .

Hence we conclude that little reliance should be placed upon the rate constants determined by the rotating sector, because the method is notoriously inaccurate when the precise mechanism of a reaction is not well defined.

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The C—C Bond Dissociation Energies in Cyclanes

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 (Received December 4, 1953)

IN a recent letter Seubold¹ has claimed to have estimated the C—C bond dissociation energies in the cyclanes from cyclopropane to cyclononane to an accuracy of approximately ± 2 kcal and, moreover, has claimed that the calculated values agree with existing experimental data. We wish to point out first that the method by which he estimates the bond strengths in cyclopropane and cyclobutane is unsuitable, and second, that he has neglected important experimental evidence on these compounds. Our objections may be summarized as follows.

1. It has been tacitly assumed that the activation energies of the reverse reactions by which the biradicals form cyclanes are zero; this is unrealistic. Seubold has estimated the heat of formation of the trimethylene and *cis*-tetramethylene biradicals in which the C—C—C bond angles are tetrahedral and hence calculated the heats of the reactions by which these radicals are formed from the cyclanes. He then identifies the heats of these reactions with the dissociation energies of the C—C bonds. However, a bond is usually said to be broken when the attraction between the two centers is of the order of kT . It is not known, and there appears to be no reliable way of estimating at what C—C—C angle the attractive force between the centers is of this order, but there is no reason to suppose that this point is reached when the angles in the radicals are exactly tetrahedral: it can hardly be so for both compounds even if it is true for one. Probably, there is still considerable strain in the radicals when the configuration is such that the bond strengths are of the order of kT , at which point the activation energies of the recombinations are zero. These strained radicals will have higher heats of formation which would yield higher values for the calculated C—C bond dissociation energies. Conversely, the reactions by which the biradicals with tetrahedral angles form cyclanes may have substantial energies of activation. An attempt to calculate this energy barrier, based on an empirical strain-energy-bond-angle relationship, led to the conclusion that it would be negligible;² this conclusion is probably invalid, however, because of the significant deviations in the cyclopropane and cyclobutane bond lengths from the alkane values,³ which were not taken into account in the calculation.

2. It is unjustifiable to correlate, as Seubold does, the low "heat of dissociation" of cyclopropane with the ease of reaction of cyclopropane and its derivatives. The isomerization of cyclopropane to propylene occurs cleanly at about 490°C with an activation energy of 65 kcal and an *A* factor of $10^{15.17}$.^{4,5} Despite the application of sensitive tests no evidence can be found for the existence of biradicals in the system;⁶ moreover, there are good theoretical reasons for supposing that the fission of the C—C bond is not the rate-determining step in the isomerization.⁷ Similarly, there is no evidence that biradicals are formed when cyclobutane decomposes to ethylene for which the activation energy is 62.8 kcal and the *A* factor $10^{15.71}$ sec⁻¹. When gases such as toluene or hydrogen are added to the reaction system, no effects compatible with the presence of free radicals are observed.^{2,8} The *A* factors for dissociation into biradicals are not likely to be less than 10^{13} sec⁻¹ in either case, so that if the proposed radical processes had activation energies of 65 and 63 kcal, respectively, the reactions would occur to the extent of about $\frac{1}{2}$ percent by such mechanisms, which would be readily observable. Thus, we should place lower limits of 65 and 63 kcal on the respective dissociation energies, at variance with our general experience of these compounds. In actual fact, such arguments tell us nothing about dissociation energies, because both radical mechanisms would show quasi-unimolecular falloff in the pressure range used for the activation energy determinations,^{4,5,9} and until the extent of such falloff is calculated, we are precluded from placing any limits on the C—C dissociation energies in cyclopropane and cyclobutane.

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THE C-C BOND DISSOCIATION ENERGY IN
CYCLOBUTANE

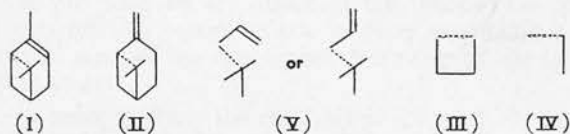
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Recently there has been some discussion¹ of the C-C bond dissociation energies in the cyclanes, particularly in cyclopropane and cyclobutane. We wish to draw attention to a method of estimating the dissociation energy of cyclobutane which has been neglected. Burwell² has proposed an ingenious mechanism to explain the products formed in the isomerization of α -pinene. Since a similar mechanism³ explains the products formed in the isomerization of β -pinene, we may have considerable confidence that it is correct. The first step in both of these mechanisms is the fission of a substituted cyclobutane ring to yield a biradical. The activation energies for the reactions which may be equated with the dissociation energies are 44⁴ and 49³ kcal. respectively. Now to a first approximation α -(I) and β -(II) pinene bear the same relation to cyclobutane (III) as propane (IV) does to 4,4-dimethyl-1-pentene (V)



: the bonds to be broken are dotted. The heats of

formation of propane and of the radicals⁵ formed from (IV) and (V) have been measured and that of 4,4-dimethyl-1-pentene may be estimated as -19.3 kcal./mole from the known⁶ heats of formation of 4-methyl-1-pentene (-11.7), 2-methylpentane (-41.7) and 2,2-dimethylpentane (-49.3). Hence it can be shown that the dissociation energies of the bonds in propane and (V) are 82 and 54 kcal./mole respectively. Therefore, if the dissociation energy of the cyclobutane bond in the pinenes is 46 kcal./mole, that in cyclobutane is $46 + 82 - 54 = 74$ kcal./mole. This may be regarded as a minimum value, for the pinene molecules are presumably more strained than cyclobutane.

If the "normal" C-C bond has a strength of 85 kcal./mole the strain energy in cyclobutane, which is 26 kcal./mole⁷, lowers the bond dissociation energy by about 11 kcal./mole. Consequently the activation energy for the internal combination of the biradical is 15 kcal.

These figures show that it is extremely unlikely that the decomposition of cyclobutane into two ethylene molecules, which has an activation energy of only 62.8 kcal. and a frequency factor of $10^{15.71}$ sec.⁻¹ involves the formation of a biradical intermediate. It is probably a straightforward molecular decomposition.

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THE PHOTOLYSIS OF HEXAFLUOROAZOMETHANE AND THE REACTIONS OF CF_3 RADICALS WITH METHANE AND *n*-BUTANE

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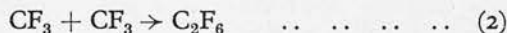
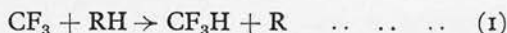
Hexafluoroazomethane was prepared by heating ICN with IF_5 in a steel bomb at 130°C .¹ after purification, the product was shown by mass-spectrographic analysis to contain only CF_3I as impurity. Photolysis of this gas at room temperature by light from an unfiltered high-pressure mercury arc yielded N_2 (9.8 vol.), C_2F_6 (1.9 vol.) and $(\text{CF}_3)_4\text{N}_2$ (7.8 vol.); at 200° , the photolysis was accompanied by a decrease in total pressure and the products contained a fairly involatile liquid $(\text{CF}_3)_2\text{N}\cdot\text{N}(\text{CF}_3)\cdot\text{N}(\text{CF}_3)\cdot\text{N}(\text{CF}_3)_2$. No appreciable amount of CF_3H was formed at either temperature provided that the reaction vessel was isolated from the vacuum system by a mercury cut-off, and even up to 350° no CF_4 was formed. However, above about 150° small amounts of CO_2 and SiF_4 were produced by the attack of CF_3 radicals on the quartz reaction vessel; attack on Pyrex was much less so that most of the experiments were carried out in a glass vessel.

In order to study the reactions of CF_3 radicals with hydrocarbons, 2 cm. of hexafluoroazomethane was photolysed in the presence of 10–20 cm. of hydrocarbon at temperatures of 30 – 350° , the ratio of CF_3H to C_2F_6 in the products being determined by mass-spectrographic analysis. The quantities of these two gases formed in any one run were very small because of the addition of the majority of the CF_3 radicals to the unsaturated hexafluoroazomethane; this addition sets serious limits on the accuracy of the method.

The results were fitted to the expression

$$k_1/k_2 = [d(\text{CF}_3\text{H})/dt] / [d(\text{C}_2\text{F}_6)/dt]^{1/2} [\text{RH}]$$

based on the assumed reaction scheme



and it was found that if $k = A \exp(-E/RT)$, $E_1 - \frac{1}{2}E_2 = 9.5 \pm 2$ kcal./mole, $A_1/A_2 \approx 3 \times 10^4$ mole⁻¹ c.c.^{1/2} sec.⁻¹ for methane and $E_1 - \frac{1}{2}E_2 = 5.5 \pm 1$ kcal./mole, $A_1/A_2 \approx 1.5 \times 10^4$ mole⁻¹ c.c.^{1/2} sec.⁻¹ for *n*-butane; it was further found that CF_3 radicals reacted with hydrogen about ten times as fast as with methane at 220° . The results suggest that the activation energies of the hydrogen abstraction reactions of CF_3 radicals are about 3 kcal./mole lower than those of the corresponding CH_3 radicals.² If A_2 is equal to the A -factor for the combination of CH_3 radicals, then the values of A_1 are very similar to those found for the corresponding CH_3 radical reactions.

It would appear difficult to improve significantly upon the accuracy of these results because the rapid addition of CF_3 radicals to hexafluoroazomethane reduces their concentration so severely that the rate of formation of C_2F_6 cannot be accurately determined; the method could however, be applied successfully if a less unsaturated source of CF_3 radicals were employed. We do not intend to investigate the present approach further.

We are very much indebted to Mr. V. W. Rowlands of the Widnes Laboratory, I.C.I. General Chemicals Division, Widnes, for carrying out the mass-spectrometer analyses.

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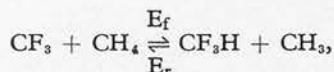
THE C-H BOND DISSOCIATION ENERGY IN FLUOROFORM

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The heat of the reversible reaction

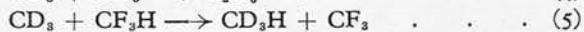


which is the difference between the C-H dissociation energies in CH_4 and CF_3H , may be obtained by measuring the difference in activation energy between the forward and reverse reactions. Recent experiments^{1,2} on the relative rates of the two reactions



have given $(E_1 - \frac{1}{2}E_2) = 9.5 \pm 2$ and 10.3 ± 0.5 kg.cal./mole, respectively; hence, using the more exact determination, $E_r = (10.3 + \frac{1}{2}E_2)$ kg.cal./mole.

We have obtained a value for E_r by measuring the activation energy of the reaction between CD_3 radicals and fluoroform in the following way. Mixtures of about 5 cm. pressure of $[\text{D}_6]$ acetone ($\sim 5\%$ $[\text{D}_5]$) and 5–20 cm. of fluoroform were photolysed at temperatures from 140–290° C. in a 250 c.c. quartz bulb; the fraction of the products volatile at liquid N_2 temperature, i.e. CO , CD_4 and CD_3H , was separated off and the ratio of $\text{CD}_3\text{H}/\text{CD}_4$ was determined mass-spectrometrically. The principal CD_3 radical reactions are



After allowing for the CD_3H formed from the hydrogen impurity in the heavy acetone (about 7–8% of the amount of CD_4 and approximately constant over the whole temperature range), the rate constant ratio

$$\frac{k_2}{k_3} = \frac{d[\text{CD}_4]/dt}{d[\text{CD}_3\text{H}]/dt} \cdot \frac{[\text{CF}_3\text{H}]}{[\text{CD}_3 \cdot \text{CO} \cdot \text{CD}_3]} = 75 \exp. (-[1800 \pm 150]/RT)$$

was obtained by applying the method of least squares to the results of ten experiments i.e. $E_3 - E_5 = 1.80 \pm 0.15$ kg.cal./mole (the error quoted being the maximum possible error of the Arrhenius plot). Direct measurements on the photolysis of $[\text{D}_6]$ acetone yield³ the value $(E_3 - \frac{1}{2}E_4) = 11.6$ kg. cal./mole (also confirmed indirectly from a comparison⁴ of the reaction of CD_3 radicals with normal and $[\text{D}_6]$ acetone); thus $E_5 = (11.6 - 1.8 + \frac{1}{2}E_4)$ kg. cal./mole. Assuming that there is no significant difference between the activation energies of the reactions of CD_3 or CH_3 radicals with fluoroform, we may identify E_5 with E_r , hence $E_r = (9.8 + \frac{1}{2}E_4)$ kg. cal./mole. Using these results,

$$\text{D}(\text{CH}_3\text{-H}) - \text{D}(\text{CF}_3\text{-H}) = E_r - E_r = 10.3 + \frac{1}{2}E_2 - 9.8 - \frac{1}{2}E_4$$

whence, if $E_2 = E_4$ and $\text{D}(\text{CH}_3\text{-H}) = 102.5 \pm 1$,

$$\text{D}(\text{CF}_3\text{-H}) = 102.0 \pm 2 \text{ kg. cal./mole.}$$

From a comparison of the heats of formation of CF_3Cl ,⁵ CH_4 and CH_3Cl we can estimate $\Delta H_f(\text{CF}_3\text{H})$ to be -169 kg. cal./mole which leads to a value of $\Delta H_f(\text{CF}_3) = -119$ kg. cal./mole; combining this with $\Delta H_f(\text{C}_2\text{F}_6) = -303$ kg. cal.⁵ gives $\text{D}(\text{CF}_3\text{-CF}_3) = 65$ kg. cal./mole.

Our results may also be used to gain some information about the combination of CF_3 radicals. From the work of Ayscough, Polanyi and Steacie,² and Whittle and Steacie,³ we have $A_1/A_2^{\frac{1}{2}} = 9.7 \times 10^3$ and $A_3/A_4^{\frac{1}{2}} = 1.2 \times 10^5$ mole⁻¹ c.c.^{1/2} sec.^{-1/2}, respectively, and from the present work $A_3/A_5 = 75$. The entropy change in reaction 1 must be very small indeed so that A_f must equal A_r , whence $A_4 \approx 35A_2$ if A_r and A_5 are assumed to be the same.

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THE REACTIONS OF METHYLENE

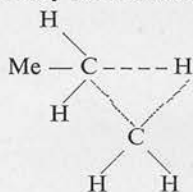
By J. H. Knox and A. F. Trotman-Dickenson

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Recent investigations of systems containing methylene indicate that this radical reacts directly with paraffin hydrocarbons to yield the next higher homologue. For example, with ethane



It appears that this is an elementary reaction and that no intermediate radicals are involved. The transition state may be formulated



where the bonds being formed are represented by dotted lines and the bond being broken by a broken line. No complete kinetic studies of reactions of this type have so far been published but results reported by Doering *et al.*¹ indicate that the attack of methylene on the hydrogen atoms in *n*-pentane and 2 : 3-dimethylbutane is statistical within experimental error over a considerable temperature range (-80° to 30°C). That is *n*-pentane yields *n*-hexane, 2-methylpentane and 3-methylpentane in the ratio 3 : 2 : 1, and 2 : 3-dimethylbutane yields 2 : 3-dimethylpentane and 2 : 2 : 3-trimethylbutane in the ratio 6 : 1. These results are not as would be expected on the basis of transition state theory.

At 298°A . the entropy of CH_2 may be calculated to be 47.7 e.u. on the assumption that the molecule contains two unpaired electrons and that the vibrational contribution is negligible. The entropy of the activated complex must be close to that of the hydrocarbon of the same formula after subtraction of the contribution for the rotation of one methyl

group (about 1.7 e.u.), and after making an adjustment for the change in molecular symmetry. For reaction (1) we thereby obtain a calculated A factor²

$$A_1 = 10^{10.15} \text{ mole}^{-1} \text{cm}^3 \text{sec}^{-1}$$

The calculation may be repeated for other hydrocarbons but it is more revealing to calculate the relative A factors for pairs of reactions. These quantities may be obtained experimentally with great accuracy and the calculated values involve no assumptions as to the entropy of the attacking radical. The following illustrative results have been obtained by the procedure outlined above.



Substances		Relative A Factors A_1/A_2 (calculated)
R_1H	R_2H	
Ethane	Methane	0.70
Ethane	<i>neo</i> -Pentane	1.98
<i>p</i> -Propane	<i>s</i> -Propane	4.30
<i>p</i> - <i>iso</i> Butane	<i>t</i> - <i>iso</i> Butane	22.2
<i>p</i> -2 : 3-Dimethylbutane	<i>t</i> -2 : 3-Dimethylbutane	41.0
1- <i>n</i> -Pentane	2- <i>n</i> -Pentane 3- <i>n</i> -Pentane	5.6 : 1.1 : 1.0

The attack on the different C-H bonds in the same molecule are regarded as distinct reactions and are represented by the prefixes "*p*," "*s*," "*t*," etc.

In the two cases where there is direct experimental evidence, namely 2 : 3-dimethylbutane and *n*-pentane, the calculated and experimental values show considerable discrepancies which appear to be well without both the experimental and probable theoretical errors. Considerable interest thus attaches to a more extensive study of the reactions of methylene, particularly with the simpler hydrocarbons.

Received February 1, 1957

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Mr. G. Boocock and Dr. H. O. Pritchard (*Manchester University*) and Dr. A. F. Trotman-Dickenson (*E.I. du Pont de Nemours and Co., Inc., Niagara Falls*) (*communicated*): In view of the remark made by Dr. K.E. Russell, we would like to describe some recent experiments on active nitrogen. We have followed the decay of the afterglow in a 20-l. flask at room temperature using a photomultiplier to measure the light emitted. Assuming that the glow was caused indirectly by the recombination of nitrogen atoms and that its intensity was proportional to the rate of the termolecular combination of nitrogen atoms, we intended to study the effect of adding known pressures of various foreign gases to the glowing system. We found that, in any one run, the rate of decay of the glow conformed well to the kinetic equation deduced from the assumed mechanism.

As it was not possible to reproduce the rate of decay from one run to another for any given pressure, we adopted the following procedure: the glow was started and the light intensity was followed for a period long enough to establish its rate of decay; a known pressure of nitrogen was added and the light intensity was again followed to establish the new rate of decay; then a further lot of nitrogen was added and the decay rate was again determined. In this way we showed

¹ Rayleigh, *Proc. Roy. Soc. A*, 1940, 176, 1, 16.

GENERAL DISCUSSION

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that the rate of decay was approximately proportional to the pressure of nitrogen. We then tried to determine the relative efficiencies of nitrogen and argon by initiating the glow in pure nitrogen, then adding a known pressure of argon, and later still adding the same pressure of nitrogen, following the light intensity at each stage to establish the various rates of decay. Unfortunately, the addition of about 2 mms of argon to the glowing nitrogen caused a marked colour change towards the red; reinvestigation revealed that even the addition of nitrogen changed the colour, but in this case towards the blue. We did not study the effect of temperature variation, but it is not unlikely that if pressure affects the colour of the afterglow, then the temperature will also affect it, suggesting that it is unwise to draw any conclusions from Lord Rayleigh's experiments about the possible curvature of $\log k$ against $1/T$ plots for atom combination reactions. Indeed, it is still doubtful if the combination of nitrogen atoms is being followed when the decay of the glow is studied.

most of the report, which was a description of the discharge which was used to produce the active nitrogen. We conclude that nitrogen is formed in the temperature of the reaction, and that the flow system is well suited to the study of the decay of the afterglow. The discrepancy between the present results and those of Lord Rayleigh is probably indicative of the fact that the reaction is not being followed when the decay of the glow is studied.

GENERAL DISCUSSION

Dr. H. O. Pritchard and Mr. R. G. Sowden (*Manchester University*, and Dr. A. F. Trotman-Dickenson (*E.I. du Pont de Nemours and Co., Inc., Niagara Falls*), (*communicated*): We have tried to extend our measurements on the rate of isomerization of cyclopropane at 490° C down to a pressure of about 0.005 mm using a flow technique; this pressure is a factor of 20 lower than is indicated by Dr. H. S. Johnston in fig. 6 of his paper. In our original experiments¹ the lowest pressure we could use (0.067 mm) was determined by the fact that we only had a 2-l. reaction vessel and were not able to analyze less than 60 mm³ of cyclopropane + propylene mixture. We therefore tried to obtain a sufficient sample for analysis by circulating cyclopropane, using a mercury diffusion pump, from a 20-l. reservoir at room temperature via a preheater at 450° C, through the 2-l. reaction vessel at 490° C, the pumping speed being varied from about 20-l./min to 1-l./h by inserting various capillaries (these speeds refer to the cold gas); apart from these capillaries, the system was constructed from wide-bore tubing and care was taken that there should be no significant build-up of pressure anywhere in the system. But a McLeod gauge attached directly to the reaction vessel read about 10 % low when the gas was being circulated. We were never able to adjust the system so that the rate of reaction was independent of pumping

¹ Pritchard, Sowden and Trotman-Dickenson, *Proc. Roy. Soc. A*, 1953, **217**, 563.

GENERAL DISCUSSION

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speed; at the highest pumping speeds, no measurable reaction had occurred after circulating for 24 h, indicating that the mean temperature attained by the gas was at least 40° C below that of the reaction vessel. The reaction appeared to be clean in this pressure range so long as there was no leak of air into the system and providing that all mercuric oxide deposits were removed by treatment with moist HCl vapour; both propylene and cyclopropane were unaffected by the discharge which occasionally occurred in the mercury circulating pump. Thus we conclude that although in theory the gas should heat up quite quickly to the temperature of the reaction vessel, in practice it is not a simple matter to design a flow system to work at such low pressures, for reactions of any speed; the discrepancy between the pressures measured under flowing and static conditions is probably indicative of the flaw in this type of experiment.

Proofs to:

A.F. Trotman-Dickenson,
Chemistry Department,
West Mains Road,
Edinburgh 9.

Metal-Carbon Bonds 1. The Pyrolyses of
Dimethyl Mercury and Dimethyl Cadmium.

by S.J.W. PRICE and A.F. TROTMAN-DICKENSON, Chemistry
Department, The University, Edinburgh.

Short title: Dimethyl mercury and dimethyl cadmium.

Illustrations: 2 figures



Hence, by thermochemistry, the heat of reaction



is 7.2 kcal.mole⁻¹ for mercury and 20.2 kcal.mole⁻¹ for cadmium.

These are the minimum dissociation energies for the bonds.

The thermal decompositions of dimethyl mercury and dimethyl cadmium have been studied by the toluene carrier technique between 465° and 608°C, and 469° and 571°C respectively. The progress of the reactions were followed by measuring the hydrogen, methane, ethylene and ethane formed. The results obtained with dimethyl mercury may be expressed by

$$\log_{10} k / \text{sec.}^{-1} = 13.1 - (50,100 + 1000 / 2.303RT) \text{ at } 16 \text{ mm}$$

in excellent agreement with previous determinations and with dimethyl cadmium by

$$\log_{10} k / \text{sec.}^{-1} = 11.9 - (45,800 + 1000 / 2.303RT) \text{ at } 18 \text{ mm}$$

In both cases k was markedly dependent upon the total pressure. The activation energies may be equated with the heats of reactions (1)



Hence, by thermochemistry, the heat of reaction (2)



is 7.2 kcal.mole⁻¹ for mercury and 20.2 kcal.mole⁻¹ for cadmium.

These are the minimum dissociation energies for the bonds.

Materials: Dimethyl mercury was prepared from mercuric chloride and methyl magnesium iodide². The crude product was dried

(CaH₂) and twice fractionated. The fraction boiling at 96°C at 765 mm was stored under vacuum at room temperature. Analysis by gas chromatography showed a maximum of 0.1% impurity.

Dimethyl cadmium was prepared by the action of anhydrous

Little is known of the dissociation energies of the metal-carbon bonds in the metallic alkyls. This paper describes an attempt to determine the dissociation energies of the bonds in dimethyl mercury and dimethyl cadmium by a kinetic method. It is hoped that information on other compounds will be reported in later papers. The reasons for selecting these compounds for study may be briefly stated. Methyl derivatives were selected so that the reactions of the radicals released on decomposition might be as simple as possible. Furthermore there exists a considerable body of reliable information on methyl reactions. The mercury compound was selected because it has been the subject of a comprehensive study by a very similar method¹ to the one employed in the present work. There is excellent agreement between the results obtained in the two investigations. Dimethyl cadmium was selected because of its great similarity to dimethyl mercury.

EXPERIMENTAL.

Materials.- Dimethyl mercury was prepared from mercuric chloride and methyl magnesium iodide². The crude product was dried (CaCl_2) and twice fractionated. The fraction boiling at 95°C at 758 mm was stored under vacuum at room temperature. Analysis by gas chromatography showed a maximum of 0.1% impurity.

Dimethyl cadmium was prepared by the action of anhydrous

cadmium chloride on methyl magnesium iodide³. The chloride was added from a conical flask connected to the reaction vessel by a short length of 1" diameter rubber tubing. The crude product was twice fractionated and the fraction boiling at 70.4°C at 240 mm was stored under vacuum at -123°C.

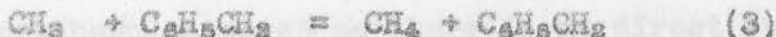
Toluene was purified by passing sulphur-free toluene twice through a quartz tube at 870°C and 25 mm pressure. The product was then fractionated and thoroughly degassed before use.

Apparatus.- The experiments were carried out in a typical toluene-carrier flow system in which the reaction zone was 155 cm³. In the runs with the vessel packed with quartz tubing the surface area in the zone was increased by a factor of five and its volume reduced to 127 cm³. The reaction products were separated in a standard low-temperature trap system and measured in a gas burette. The hydrogen was estimated by oxidation in a copper oxide tube. The ethylene content of the ethane was determined by gas chromatography (we are much indebted to Mr. J. Falconer for these analyses).

Except as noted in the tables, the flow of alkyl lasted for 30 min. during each run, preceded and followed by 5 min. flow of toluene alone. Contact times were calculated on the assumption that the ideal gas law was obeyed by all substances within the reaction zone. The rate constants were calculated from the usual first-order equation.

RESULTS AND DISCUSSION.

A possible mechanism for the decomposition of the metallic alkyls in the presence of toluene is as follows¹:



The results contained in tables 1 and 2 may be discussed in terms of this mechanism, in which it is assumed that reaction (2) is very much faster than reaction (1).

According to the mechanism the number of moles of ethane + half the number of moles of methane formed during a run should be equal to the number of moles of the alkyl which have decomposed. Using this measure of the progress of the reactions it was found that the decomposition of dimethyl cadmium obeys first order kinetics at a constant total pressure in the system (see runs 7, 8, 19, 20, 21, 30, 32, 37). In general in this work less attention was paid to the details of the dimethyl mercury decomposition. The experiments were primarily carried out to check the finding of Govenlock, Polanyi and Warhurst¹ and to extend them slightly. Experiments with dimethyl cadmium in the packed reaction vessel indicated that the

decomposition was homogeneous, as the packing caused no appreciable change in the first-order rate constant.

The proposed mechanism for the decomposition will only be valid if reaction (6) can be neglected as a possible



means by which methyl radicals might be removed from the system.

k_6 has not been measured so there is no direct evidence on this

point. Two facts, however, have been established, neither of which is compatible with reaction (6) ^{being} very important in this system.

First, the rate constants, as derived, are independent of the rate of release of methyl radicals into the system; this has been checked by using various pressures of dimethyl cadmium while keeping the other conditions constant. Second, a run carried out at 595°C with a contact time of 5.6 sec. produced methane and ethane in quantities corresponding to 98.7% decomposition of the alkyl; this showed that no methyl radicals were removed by side reactions. Furthermore, the A factor of reaction (6) may be calculated from the results of Szwarc⁵ and reasonable estimates of the entropies of the methyl and benzyl radicals⁶. Hence it is found that $A_6 = 10^{9.5} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ which is the maximum possible value of k_6 . A reaction with such a low rate constant cannot compete successfully with reactions (3) or (4).

The rate constants for the decompositions depend markedly on the

total pressure in the reaction system. This is shown in Fig. 1. The reactions are obviously being investigated under conditions such that the rate of energy transfer is not sufficient to maintain the high pressure rate constant. This is to be expected for molecules containing only three heavy atoms. Accordingly the majority of the runs with each alkyl were done near one pressure and corrected to this selected pressure by making use of the empirically determined relation between the rate constants and the pressure.

Values of $k_3/k_4^{1/2}$ were derived from the quantities of methane and ethane formed and the pressure of toluene. It was found that this ratio also depended upon pressure as is shown in Fig. 1. The variation must be ascribed to the variation in k_4 as k_3 should not depend upon pressure. This variation of k_4 with pressure has been observed in studies of the photolysis of acetone at lower temperatures but also at lower pressures,^{7,8}. This is in qualitative agreement with the predictions of the theory of unimolecular reactions⁹.

Arrhenius plots of the rate constants are given in Fig. 2.

The straight lines correspond to:

$$\log_{10} k_1 / \text{sec.}^{-1} = 13.1 - (50\,100 \pm 1000 / 2.303RT)$$

for dimethyl mercury at 16 mm pressure;

$$\log_{10} k_1 / \text{sec.}^{-1} = 11.9 - (45\,800 \pm 1000 / 2.303RT)$$

for dimethyl cadmium at 18 mm pressure

$$\log_{10} (k_3/k_4^{1/2}) / \text{mole}^{-1/2} \text{ cm}^{3/2} \text{ sec.}^{-1/2} = 6.4 - (13\,500 / 2.303RT).$$

The results with dimethyl mercury are in excellent agreement with those of earlier workers.

The consequences of studying the reactions at pressures at which the rates are a function of pressure must be examined before certain conclusions can be drawn from these results. High pressure A factors cannot be deduced; the true A factors may be anything up to ten times the A factors in these Arrhenius equations. Activation energies depend much less markedly upon pressure. The activation energies at high pressures are unlikely to be more than 1 kcal greater than those given here. $E_4 = 0 \text{ kcal. mole}^{-1}$ at high pressures, consequently it should have a negative value (though probably a small one) under the present conditions. E_4 would certainly not be expected to be sufficiently low to reconcile the present values of $k_3/k_4^{1/2}$ with those determined at lower temperatures^{10,11}. Probably the values given here are not very reliable because of difficulties associated with the precise definition of the reaction volume.

The sum of the bond strengths in these metallic alkyls may be calculated from their heats of formation and that of the methyl radical. There is still some doubt as to the precise strength of the C-H bond in methane. $D(\text{CH}_3\text{-H})$ may however be conveniently taken to be $102.5 \text{ kcal. mole}^{-1}$; no error need then be assigned to this value; if it is subsequently shown to be wrong the present

calculations may readily be adjusted. If the measured activation energies are equated with the dissociation energies of the first methyl-carbon bonds (D_1), the following table may be compiled:

Alkyl	ΔH_f° (gas) kcal.mole ⁻¹	D_1+D_2 kcal.mole ⁻¹	D_1 kcal.mole ⁻¹	D_2 kcal.mole ⁻¹
Hg(CH ₃) ₂	22.4	57.3 ^{11,12}	50.1	7.2
Cd(CH ₃) ₂	25.2	66.8 ¹³	45.8	21.0

In constructing this table two assumptions are tacitly made.

First, that the metal atom released in the decomposition is in its ground electronic state. Second, that the addition of a methyl radical to a metal atom (reaction-2) is a process with zero energy of activation. Either of both of these assumptions may be invalid.

D_2 must therefore be regarded as a minimum value. On the other hand these values of $D(X-CH_3)$ are high compared with the known values of $D(X-H)$, that is for mercury and kcal.mole⁻¹ for cadmium¹⁴. A full discussion of the significance of these results may be postponed until more metallic alkyls have been investigated.

Table 1. The Pyrolysis of Dimethyl Mercury.

Run	Temp. (°C)	Contact time (Sec.)	Toluene (mm)	HgMe ₂ (10 ⁻⁴ mole)	CH ₄ (10 ⁻⁴ mole)	C ₂ H ₂ (10 ⁻⁴ mole)
a	560	1.35	17.0	4.55	5.46	0.38
a	560	1.37	16.1	12.00	12.50	1.57
a	543	1.39	16.1	14.90	11.50	1.49
a	542	1.44	16.0	12.90	10.06	1.15
a	585	1.33	16.5	13.40	15.50	2.06
a	531	1.41	16.3	15.30	8.82	1.09
a	505	1.45	16.2	15.20	3.90	0.39
a	483	1.52	16.2	14.20	1.60	0.12
a	465	1.51	16.1	16.20	0.71	0.04
a	466	1.52	16.1	14.60	0.69	0.05
c	608	.405	16.0	3.42	4.49	0.19
b, c	585	.425	16.2	6.71	7.50	0.48
c	573	.459	16.1	7.80	6.59	0.58
c	562	.435	16.1	10.30	6.80	0.56
c	562	.426	16.5	10.40	7.12	0.58
c	562	.425	16.1	21.10	12.40	1.61
c	543	1.72	10.3	15.60	10.30	2.30
c	543	2.28	4.4	12.10	6.36	2.70
c	543	1.13	25.5	14.10	12.00	1.16

a: H₂ 1-0.5% C₂H₄ ca. 0.5% of C₁ and C₂ fractions.

b: H₂ nil

c: Length of run 20 min.

Table 2. The Pyrolysis of Dimethyl Cadmium.

Temp. (°C)	Contact time (sec.)	Toluene (mm)	CdMe ₂ (10 ⁻⁴ Mole)	CH ₄ (10 ⁻⁴ mole)	C ₂ H ₆ (10 ⁻⁴ mole)
552	0.93	15.6	1.52	0.88	0.11
552	1.10	15.6	18.70	12.60	1.55
552	1.30	19.2	9.20	8.90	0.57
552	1.02	18.7	48.80	28.50	6.70
552	1.23	5.2	27.40	10.80	5.64
552	1.03	24.4	9.66	10.50	0.41
552	0.59	21.8	25.60	15.90	1.15
552	0.74	13.2	17.20	8.60	1.28
552	0.63	15.4	26.60	14.40	1.74
552	0.68	13.8	21.60	11.10	1.55
552	0.83	14.4	14.90	8.40	1.34
552	1.72	18.0	19.30	18.60	2.22
552	1.73	18.6	19.30	17.80	2.31
552	0.62	18.6	16.30	8.85	0.87
552	1.37	20.0	3.78	3.94	0.16
552	2.13	6.3	18.10	10.90	3.48
552	1.71	10.0	19.90	15.40	3.70
552	2.08	5.8	22.20	12.30	6.06
571	1.38	17.0	17.30	19.00	2.70
524	1.43	18.3	14.40	6.83	0.68
490	1.47	17.5	23.00	3.64	0.32
469	1.72	18.6	24.90	2.20	0.17
469	5.55	19.9	14.90	3.62	0.47

Table 2 continued.

Temp. (°C)	Contact time (sec.)	Toluene (mm)	CdMe ₂ (10 ⁻⁴ Mole)	CH ₄ (10 ⁻⁴ mole)	C ₂ H ₆ (10 ⁻⁴ mole)
501	5.57	18.5	14.30	8.34	1.65
524	3.47	16.5	19.90	14.80	3.30
522	4.03	17.6	10.70	9.60	0.93
490	5.05	19.3	21.20	8.48	2.16
469	6.60	19.3	20.00	5.30	0.87
571	0.64	17.0	22.22	17.80	2.23
517	3.42	18.9	19.10	12.80	2.17
508	3.00	19.0	24.20	10.70	1.97

a: complete analysis CH₄ 82.6%, C₂H₆ 15.9%, H₂ 0.8%, C₂H₄ 0.7%

b: packed vessel

c: H₂ 1.25 ± 0.25% of C₁ fraction.

d: Length of run 20 mins

Table 2 continued.

Run No.	Temp. (°C)	Contact time (sec.)	Toluene (mm)	CdMe ₂ (10 ⁻⁴ Mole)	CH ₄ (10 ⁻⁴ mole)	C ₂ H ₆ (10 ⁻⁴ mole)
33a	501	5.57	13.5	14.30	8.34	1.65
34	524	3.47	16.5	19.90	14.80	3.30
35	522	4.03	17.6	10.70	9.60	0.93
36	490	5.05	19.3	21.20	8.48	2.16
37	469	6.60	19.3	20.00	5.30	0.87
38c	571	0.64	17.0	22.22	17.80	2.23
39b	517	3.42	18.9	19.10	12.80	2.17
40b	508	3.00	19.0	24.20	10.70	1.97

a: complete analysis CH₄ 32.6%, C₂H₆ 15.9%, H₂ 0.8%, C₂H₄ 0.7%

b: packed vessel

c: H₂ 1.25 ± 0.25% of C₁ fraction.

d: Length of run 20 mins

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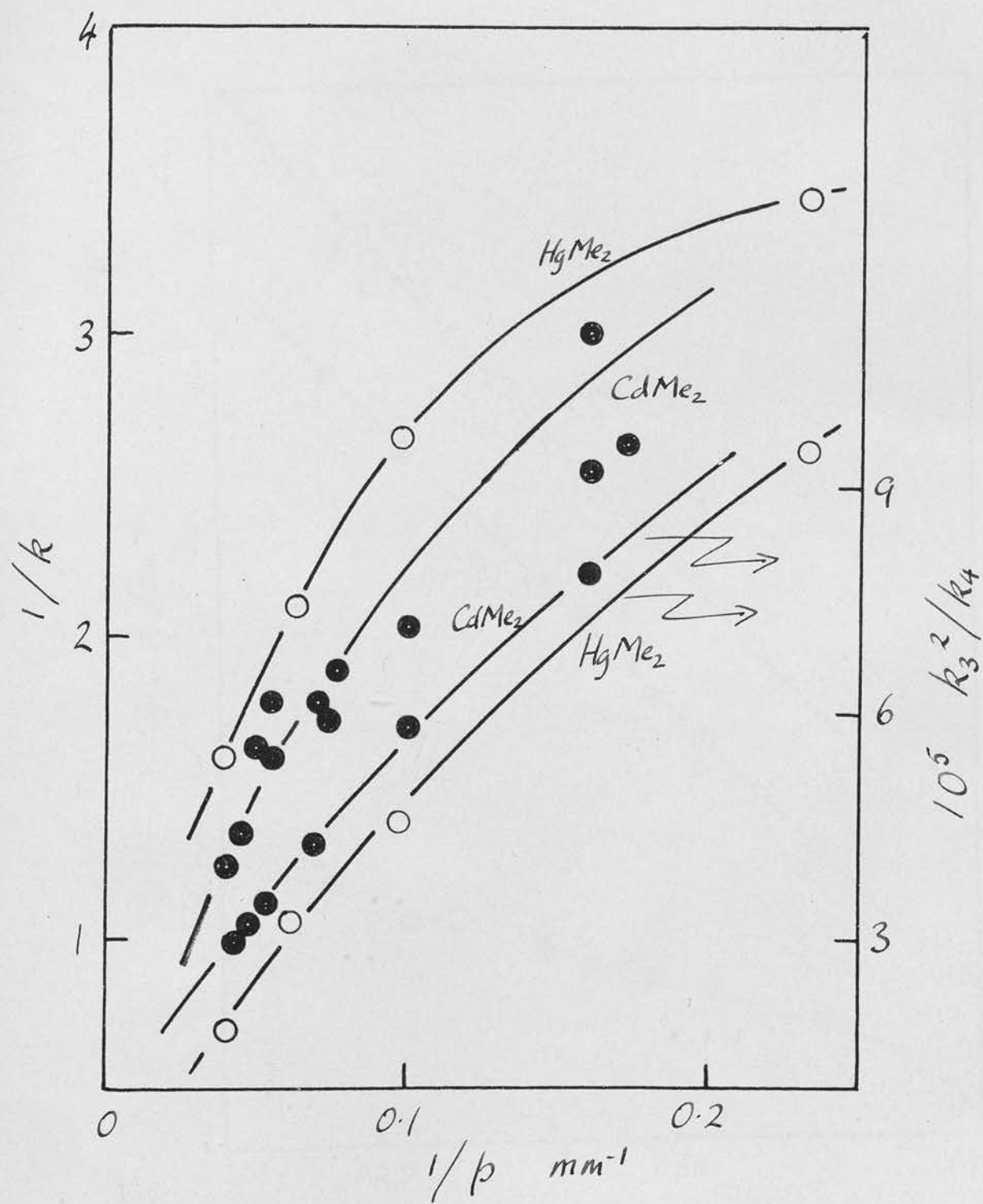


Fig 1

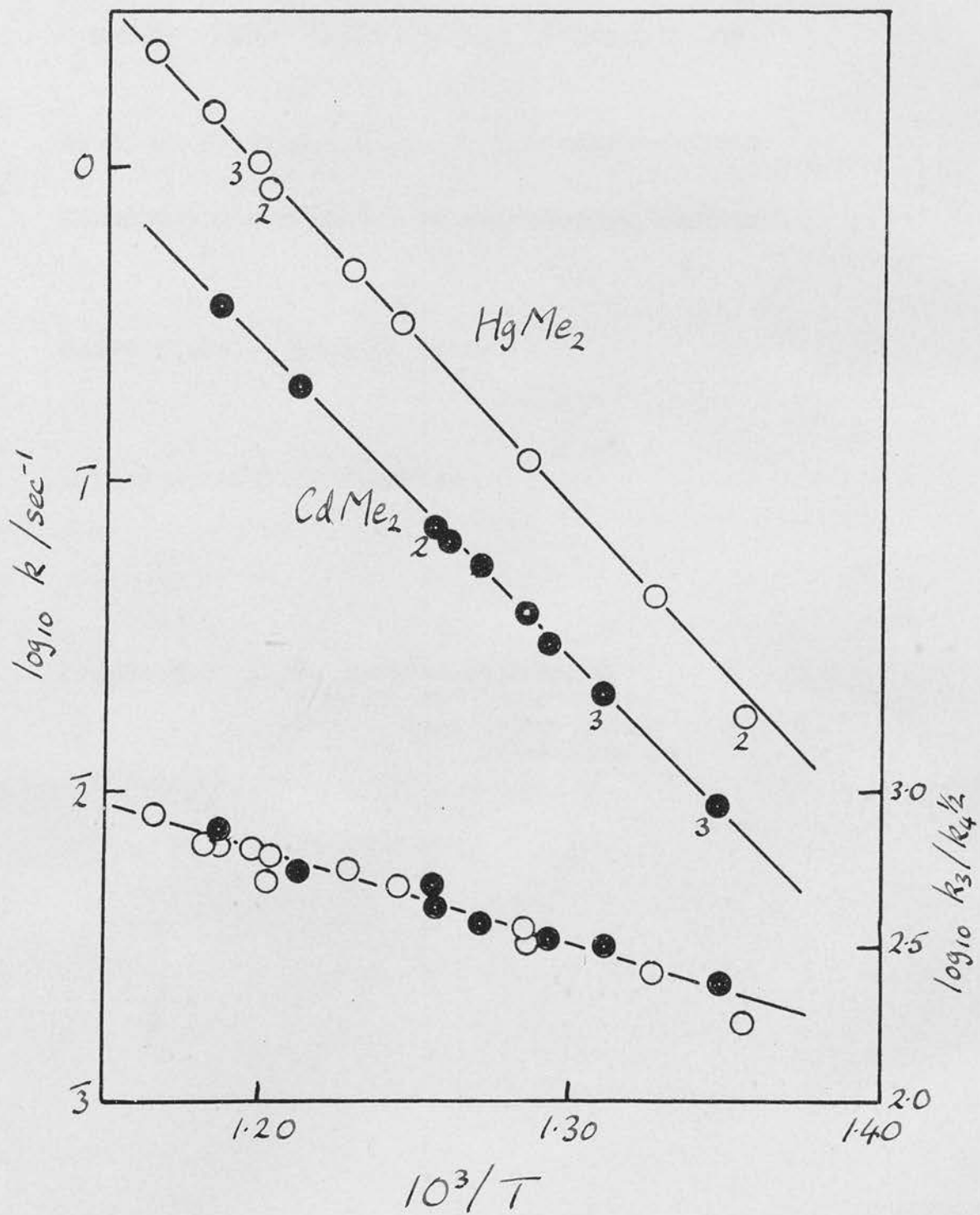


Fig 2

METAL-CARBON BONDS 2. THE PYROLYSIS OF
DIMETHYL ZINC.

by S. J. W. Price and A. F. Trotman-Dickenson

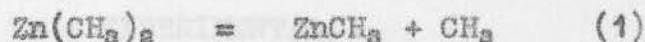
Chemistry Department, The University, Edinburgh.

Short title: Dimethyl Zinc.

Illustrations: 2 figures.

Proofs to: A. F. Trotman-Dickenson,
Chemistry Department,
West Mains Road,
Edinburgh, 9.

The thermal decomposition of dimethyl zinc has been studied by the toluene carrier technique between 573 and 827°C. The progress of the reaction was followed by measuring the hydrogen, methane, ethylene and ethane formed. The decomposition occurs in two steps



$$\log_{10} k_1 / \text{sec.}^{-1} = 11.25 - (47200 \pm 1000 / 2.303 \text{ RT}) \text{ at } 16 \text{ mm.}$$

$$\log_{10} k_2 / \text{sec.}^{-1} = 6.8 - (35000 / 2.303 \text{ RT}) \text{ at } 16 \text{ mm.}$$

Both rate constants are markedly dependent on the pressure in the system. The activation energies may be equated with the bond strengths, hence $D_1 = 47.2$, $D_2 = 35$, $D_1 + D_2 = 82$ kcal.mole⁻¹. Thermochemistry yields $D_1 + D_2 = 82.9$ kcal.mole⁻¹.

RESULTS AND DISCUSSION

The complete experimental results are given in Table I. Their satisfactory interpretation depends upon the selection of the correct mechanism for the system.

The first paper in this series¹ described the thermal decomposition of dimethyl mercury and dimethyl cadmium.

The present paper on the decomposition of dimethyl zinc completes the study of the alkyls of suitable group II metals. No previous investigation of this pyrolysis has been reported.

EXPERIMENTAL.

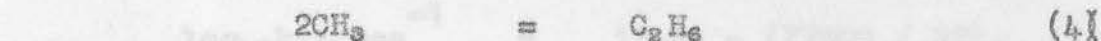
MATERIALS. - Dimethyl zinc was prepared by the reaction of methyl iodide with a freshly prepared zinc-copper couple^{2,3}. Traces of methyl iodide were removed from the crude product by passing the vapour five times over a fresh portion of the couple at 150°C. A fraction boiling between 46.4° and 46.5°C. at 758 mm. was collected. Three weighed samples were decomposed with air-water or air alone and the residual methyl iodide determined by gas chromatography. Not all the methyl iodide was removed but it amounted to considerably less than 1% of the samples. The alkyl was stored under vacuum at -196°C.

APPARATUS. - The apparatus and procedure were essentially the same as those employed in Part 1¹.

RESULTS AND DISCUSSION.

The complete experimental results are given in Table 1. Their satisfactory interpretation depends upon the selection of the correct mechanism for the system.

It was expected that the mechanism for the decomposition of dimethylzinc would be very similar to that for the decomposition of dimethyl mercury and dimethyl cadmium:



The XCH_3 radical formed by the other two alkyls decomposed so rapidly that it could be assumed that two methyl radicals were formed from each molecule that underwent reaction (1). However, it was soon found that this assumption was not tenable for dimethyl zinc. It appeared that even as high as 670°C . reaction (2) did not occur to any great extent under the prevailing conditions. Only above 730°C . was reaction (2) an important source of methyl radicals. Accordingly the decompositions of dimethyl zinc and methyl zinc were treated as successive reactions. At the highest temperatures all the dimethyl zinc was converted to methyl zinc in a very small fraction of the contact time. The rate of decomposition of methyl zinc could then readily be determined; the only interference came from the decomposition of the toluene carrier. At low temperatures the decomposition of methyl zinc was negligible and the decomposition of dimethyl zinc could be simply treated as a unimolecular reaction yielding one methyl radical. At intermediate temperatures the appropriate treatment for successive reactions of comparable rate had to be applied. The detailed methods of calculating were as

as follows:

(a) The high temperature ranges (k_2). The amount of CH_4 produced was found by analysis of the $\text{CH}_4\text{-H}_2$ fraction, a correction then had to be applied for the CH_4 produced by the decomposition of the toluene carrier. This correction was obtained from Szwarc's⁴ expression for the rate constant

$$\log_{10} k / \text{sec}^{-1} = 13.5 - (77500 / RT),$$

assuming that the ratio of $\text{H}_2 : \text{CH}_4$ produced was in the ratio of 1.5 : 1. An experiment on the pyrolysis of pure toluene at 783°C . yielded a value of k in good agreement with this expression; the ratio $\text{H}_2 : \text{CH}_4$ was exactly 1.5 : 1. The percentage decomposition of methyl zinc was then equal to

$$\frac{\text{corrected moles of methane} + 2 \times \text{moles of ethane} \times 100}{\text{moles of dimethyl zinc used.}} - 100$$

First-order rate constants were calculated from these percentage decompositions. This calculation implies that the dimethyl zinc is converted to methyl zinc immediately it enters the reaction zone.

(b) The low temperature range (k_1). k_1 was calculated from the usual formula for successive unimolecular reactions:

$$\text{CH}_4 + 2\text{C}_2\text{H}_6 = \text{Zn}(\text{CH}_3)_2 \text{ used } \left\{ 2 - \frac{k_1}{k_1 - k_2} (e^{-k_1 t} + e^{-k_2 t}) \right\}$$

The equation was solved for k_1 by the method of successive approximations. The values obtained were not very sensitive to the value selected for k_2 as the percentage decomposition of the ZnCH_3 was of the order of 1% at 597°C ., 3% at 648°C . and 6% at 701°C .

The method of calculation depends upon the assumption that the zinc methyl radicals which do not decompose do not react in any other way while within the decomposition reaction zone. Presumably they eventually form stable saturated molecules in some cooler portion of the apparatus. No alternative assumption that was in accordance with the experimental findings and involved plausible reactions could be discovered.

the Arrhenius ratio by a factor of five had no appreciable effect on the rates as is shown in Figure 2. So that the rate constants might be comparable, all that were determined in the region of 16 mm. pressure were corrected empirically to 16 mm. pressure. The resulting values of the rate constants, together with four determined at 5 mm. pressure, are plotted on an Arrhenius diagram (Fig. 2). At 16 mm. total pressure

$$\log_{10} k_1 / \text{sec}^{-1} = 11.25 - (47200 \pm 1000/RT)$$

$$\log_{10} k_2 / \text{sec}^{-1} = 6.36 - (35000/RT), \text{ and at low temperatures}$$

$$\log_{10} (k_1/k_2) / \text{atm}^{3/2} \text{ sec}^{-1} = 6.30 - (13000/RT).$$

At 5 mm. total pressure

$$\log_{10} k_1 / \text{sec}^{-1} = 11.05 - (47300/RT)$$

The values of k_1 and k_2 at infinite pressure could only be determined from experiments over a far wider range of pressures than could be reached with our apparatus. Reaction (2) was apparently studied in its 'second-order' region; that is, k_2 is directly proportional to the total pressure as is shown in Fig. 1. If toluene and zinc methyl are equally effective in energy transfer, then the rate

The ratios $k_3/k_4^{1/2}$ were determined in the usual way assuming that the reactions took place uniformly throughout the reaction zone.

The rate constants k_1 , k_2 and the ratio $k_3/k_4^{1/2}$ were found to be markedly dependent upon the total pressure in the reaction system, as shown in Fig. 1. This was not due to any heterogeneous reaction. Packing the vessel with silica tubing so as to increase the surface:volume ratio by a factor of five had no appreciable effect on the rates as is shown in Figure 2. So that the rate constants might be comparable, all that were determined in the region of 16 mm. pressure were corrected empirically to 16 mm. pressure. The resulting values of the rate constants, together with four determined at 5 mm. pressure, are plotted on an Arrhenius diagram (Fig. 2). At 16 mm. total pressure

$$\log_{10} k_1 / \text{sec}^{-1} = 11.25 - (47200 \pm 1000/RT)$$

$$\log_{10} k_2 / \text{sec}^{-1} = 6.86 - (35000/RT), \text{ and at low temperatures}$$

$$\log_{10} (k_3/k_4^{1/2}) / \text{mole}^{-1/2} \text{cm.}^{3/2} \text{sec}^{-1/2} = 6.30 - (13000/RT).$$

At 5 mm. total pressure

$$\log_{10} k_1 / \text{sec}^{-1} = 11.03 - (47300/RT)$$

The values of k_1 and A_1 at infinite pressure could only be determined from experiments over a far wider range of pressures than could be reached with our apparatus. Reaction (2) was apparently studied in its 'second-order' region; that is, k_2 is directly proportional to the total pressure as is shown in Fig. 1. If toluene and zinc methyl are equally effective in energy transfer, then the rate

constant may be written

$$\log_{10} k_2 / \text{mole}^{-1} \text{cm.}^3 \text{sec}^{-1} = 13.36 - (35000/RT)$$

The values of $k_3/k_4^{1/2}$ obtained at high temperatures are clearly not consistent with those at lower temperatures. The reliability of both sets of determinations of the rate constants is doubtful because of the difficulty of defining the reaction zone. However, the low temperature results and the variation with pressure are in excellent agreement with those obtained with dimethyl mercury and dimethyl cadmium¹.

The tests which can be applied in a flow system to demonstrate the adequacy of a mechanism are rather limited. This is especially so when, as in the present case, the rates of the unimolecular reactions are partially determined by the rate of energy transfer. Those tests which were applicable confirmed the mechanism.

From the quantity of methane (corrected) and ethane formed it was deduced that 98% of the possible number of methyl radicals were released in passing dimethyl zinc through the system at 842°C. with a contact time of 6 seconds. The proportion that may be derived from the rate constants given above is 98.5%. This is direct evidence that reaction (6) is unimportant. As a further check the



contact time was varied by approximately a factor of ten in one series of runs (1 - 15).

The rather large quantities of hydrogen formed at the higher

temperatures were not all the products of the unimolecular decomposition of toluene. It is possible that they were formed by the decomposition of benzyl radicals and of dibenzyl. A small quantity is probably formed by the decomposition of ethane into ethylene and hydrogen. For this reason the ethylene was treated as ethane in calculating the rate constants. If this is unjustifiable the error introduced is small because the C_2 fraction is much smaller than the amount of methane.

The apparent activation energy of a unimolecular reaction is a function of the pressure at which it is determined if the rate of the reaction is itself a function of pressure. However, for small molecules the difference between the activation energies determined in the 'second order' region and at high pressures is not great. Until more information is available it is reasonable to suppose that the activation energies found at 16 mm. differ little from the high pressure values. These activation energies may be equated with the heats of reaction if the back reactions (combination of atoms and radicals) have no activation energies. On this assumption the following values of the bond strengths may be obtained

$$\underline{D}(\text{CH}_3 - \text{ZnCH}_3) = \underline{D}_1 = 47.2 \pm 1 \text{ k cal.mole}^{-1}$$

$$\underline{D}(\text{Zn} - \text{CH}_3) = \underline{D}_2 = 35 \text{ k cal.mole}^{-1}$$

No useful estimate of the probable error of the second value can be made (3 to 5 k cal.mole⁻¹ is probably a fair figure).

$$\text{Hence, } \underline{D}_1 + \underline{D}_2 = 82 \text{ k cal.mole}^{-1}$$

This quantity may also be derived from the heat of formation of dimethyl zinc⁵ ($-13.3 \text{ k cal.mole}^{-1}$), of the zinc atom and of the methyl radical (based upon $\underline{D}(\text{CH}_3 - \text{H}) = 102.5 \text{ k cal.mole}^{-1}$). From these quantities

$$\underline{D}_1 + \underline{D}_2 = 82.9 \text{ k cal.mole}^{-1}.$$

The agreement with the kinetic estimate is meaninglessly good as errors of $\pm 4 \text{ k cal.mole}^{-1}$ should be assigned to both figures. However, they do indicate that when dimethyl zinc decomposes, the zinc atom is released in its ground state.

The results which have been obtained from our studies of the pyrolysis of the dimethyl compounds of the group II metals may be summarized as follows:

	\underline{D}_1	$\underline{D}_1 + \underline{D}_2$ k cal.mole ⁻¹	\underline{D}_2	$\underline{D}(\text{X} - \text{H})^6$
Hg(CH ₃) ₂	50	57.3 *	7	9
Cd(CH ₃) ₂	46	66.8 *	21	16
Zn(CH ₃) ₂	47	82(82.9) *	35	20

*from thermochemistry assuming $\underline{D}(\text{CH}_3 - \text{H}) = 102.5 \text{ k cal.mole}^{-1}$.

A full discussion of these figures may be postponed until more experimental results are available. It is, however, interesting in connection with the problem of $\underline{D}(\text{CH}_3 - \text{CO})$ and $\underline{D}(\text{H} - \text{CO})$ to note that for cadmium and zinc $\underline{D}(\text{X} - \text{CH}_3)$ is greater than $\underline{D}(\text{X} - \text{H})$.

Table 1. The Pyrolysis of Dimethyl Zinc.

1. Price and Trotman-Dickenson, Trans. Faraday Soc., 1957.
2. Renshaw and Greenlaw, J. Amer. Chem. Soc., 1920, 42, 1472.
3. Bamford, Levi and Newitt, J. Chem. Soc., 1946, 68, 468.
4. Szwarc, J. Chem. Phys., 1948, 16, 128.
5. Long and Norrish, Phil. Trans., 1949, 241A, 587.
6. Cottrell, The Strength of Chemical Bonds.

597	5.5	0.30	8.58	1.90	-	18.0
597	16.5	1.13	3.72	0.04	-	16.3
597	5.8	1.50	4.04	0.13	-	18.2
597	4.5	1.44	2.76	0.19	-	19.1
597	10.0	1.17	3.60	0.13	-	18.4
597	16.5	0.96	19.36	0.61	-	72.0
597	16.5	0.97	6.32	0.15	-	35.5
648	16.5	0.94	12.00	0.20	0.10	19.0
672	16.8	0.89	16.50	0.28	0.15	20.0
672	16.5	0.90	16.20	0.31	0.15	19.6
672	5.8	1.14	13.85	0.65	0.10	19.5
672	5.3	1.13	13.60	0.70	0.10	19.2
672	16.4	0.91	15.60	0.25	0.15	18.1
701	16.5	0.86	16.20	0.30	0.30	18.5
701	16.5	0.86	17.10	0.34	0.50	17.7
701	16.0	0.87	18.10	0.37	0.30	18.5
624	16.0	0.93	4.50	0.05	-	13.9
672	16.5	0.75	14.00	0.26	0.40	18.4
624	16.2	0.84	7.30	0.28	-	21.1

Table 1. The Pyrolysis of Dimethyl Zinc.

Run No.	Temp. °C.	Toluene (mm)	t (sec)	CH ₄	C ₂ H ₆	H ₂	ZnMe ₂
				10 ⁻⁴ mole			
1	597	22.4	6.74	14.40	0.73	-	18.2
2	597	12.5	9.00	11.70	1.25	-	17.1
3	597	7.2	10.85	9.46	2.41	-	17.3
4	597	28.5	4.91	13.50	0.40	-	17.4
5	597	16.0	4.73	11.00	0.57	-	17.9
6	597	9.8	5.66	9.34	0.94	-	16.8
7	597	26.5	3.53	10.70	0.27	-	17.1
8	597	6.6	6.30	8.58	1.50	-	18.0
9	597	16.5	1.13	3.72	0.04	-	18.3
11	597	5.8	1.50	4.04	0.13	-	18.2
12	597	4.6	1.44	2.76	0.19	-	19.1
13	597	10.0	1.17	3.60	0.13	-	18.4
14	597	16.5	0.98	12.36	0.61	-	72.0
15	597	16.5	0.97	6.32	0.16	-	35.5
17	648	16.6	0.94	12.00	0.20	0.10	19.0
18	672	16.8	0.89	16.60	0.28	0.15	20.0
19	672	16.3	0.90	16.20	0.31	0.15	19.6
20	672	5.8	1.11	13.85	0.65	0.10	19.5
21	672	5.3	1.15	13.60	0.70	0.10	19.2
22	672	16.4	0.91	15.80	0.25	0.15	18.1
23	701	16.6	0.86	18.20	0.30	0.30	18.5
24	701	16.5	0.86	17.10	0.31	0.30	17.7
25	701	16.0	0.87	18.10	0.37	0.30	18.5
29	624	16.0	0.93	4.90	0.05	-	13.9
30 ^a	672	16.3	0.75	14.00	0.26	0.10	18.4
31 ^a	624	16.2	0.84	7.30	0.28	-	21.1

Table 1. (cont.)

32 ^a	672	16.1	0.78	14.50	0.32	0.10	18.9
33 ^a	701	16.1	0.74	17.40	0.39	0.20	18.8
40	658	16.3	1.06	12.55	0.29	0.15	17.0
41	658	16.3	0.99	12.10	0.21	0.15	17.0
42	573	16.0	1.10	1.18	0.01	-	12.9
43	700	16.6	0.90	17.30	0.23	0.30	17.1
26	730	16.6	1.01	19.9	0.44	0.60	18.2
27	730	16.3	1.04	19.9	0.47	0.60	18.7
34 ^a	755	16.8	0.72	21.6	0.56	3.00	19.7
35 ^a	793	16.8	1.28	25.8	1.40	4.10	19.4
36 ^a	793	16.4	0.73	23.3	0.90	6.90	19.1
37 ^a	825	16.0	0.71	25.3	1.02	11.90	18.7
38	827	16.0	0.90	24.7	0.97	11.90	17.8
39	762	16.3	0.88	19.5	0.49	2.70	16.7
44	758	16.1	0.89	19.1	0.60	2.20	17.2
45 ^c	783	15.8	0.89	27.8	1.52	4.70	20.6
47	783	6.3	0.60	20.4	0.80	2.60	17.7
48 ^b	783	9.5	1.27	22.5	1.03	3.20	17.2
49	783	15.8	0.95	25.8	0.77	5.70	16.9
50	783	16.2	0.97	7.96	0.31	3.04	5.7
51 ^c	825	16.2	0.91	16.85	0.71	8.95	11.2

a: Runs in packed reaction vessel.

b: Complete analysis (10^{-4} mole) CH_4 : 22.5, C_2H_6 : 0.31

c: Run 20 minutes. H_2 : 3.20, C_2H_4 : 0.72

CAPTIONS.

Fig. 1. The variation of the rate constants with pressure. Open circles: the decomposition of dimethyl zinc (597°C.). ~~Squares~~: the decomposition of methyl zinc (783°C.). Full circles: k_4/k_3^2 (597°C.).

Fig. 2. Arrhenius plots for the decomposition of dimethyl and methyl zinc and the reaction of methyl radicals with toluene. The figures beside the points indicate the number of runs averaged to obtain the value plotted; superscripts, runs in a packed vessel; subscripts, runs in an unpacked vessel. Full circles: $k_3/k_4^{1/2}$.

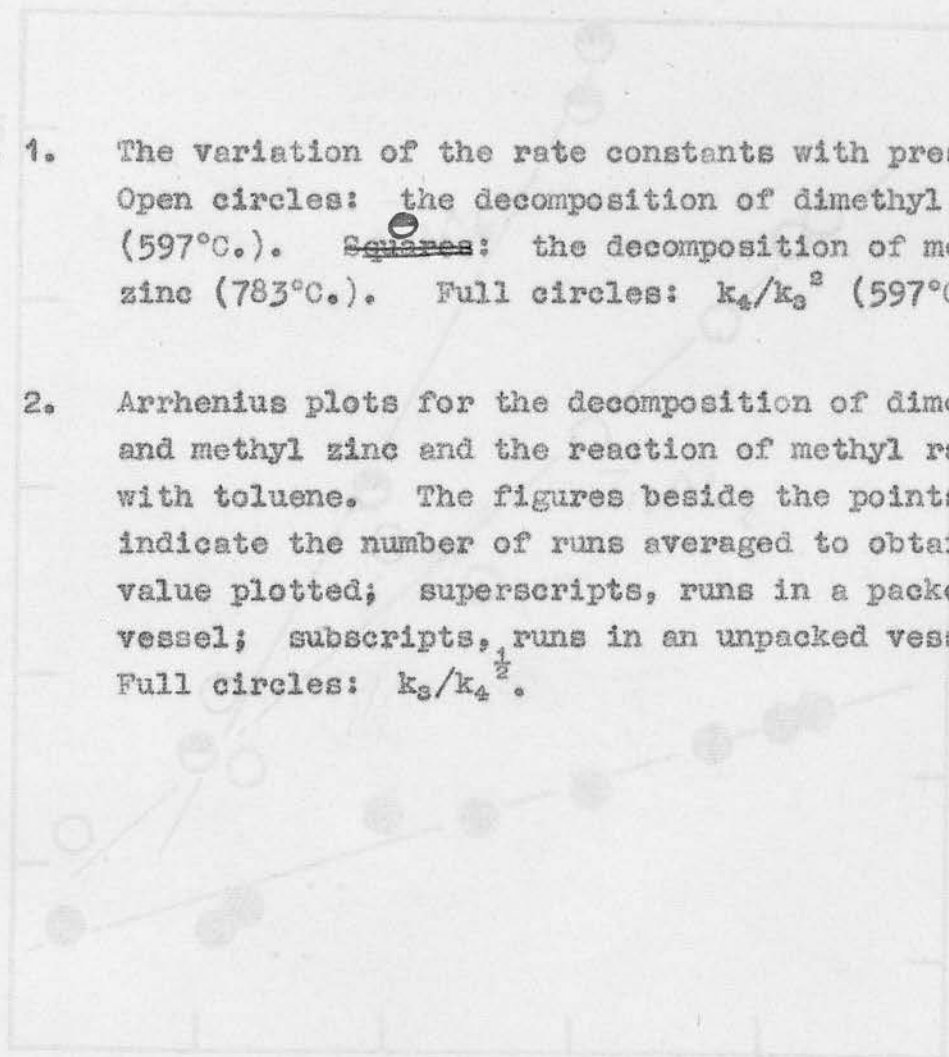


Fig. 1.

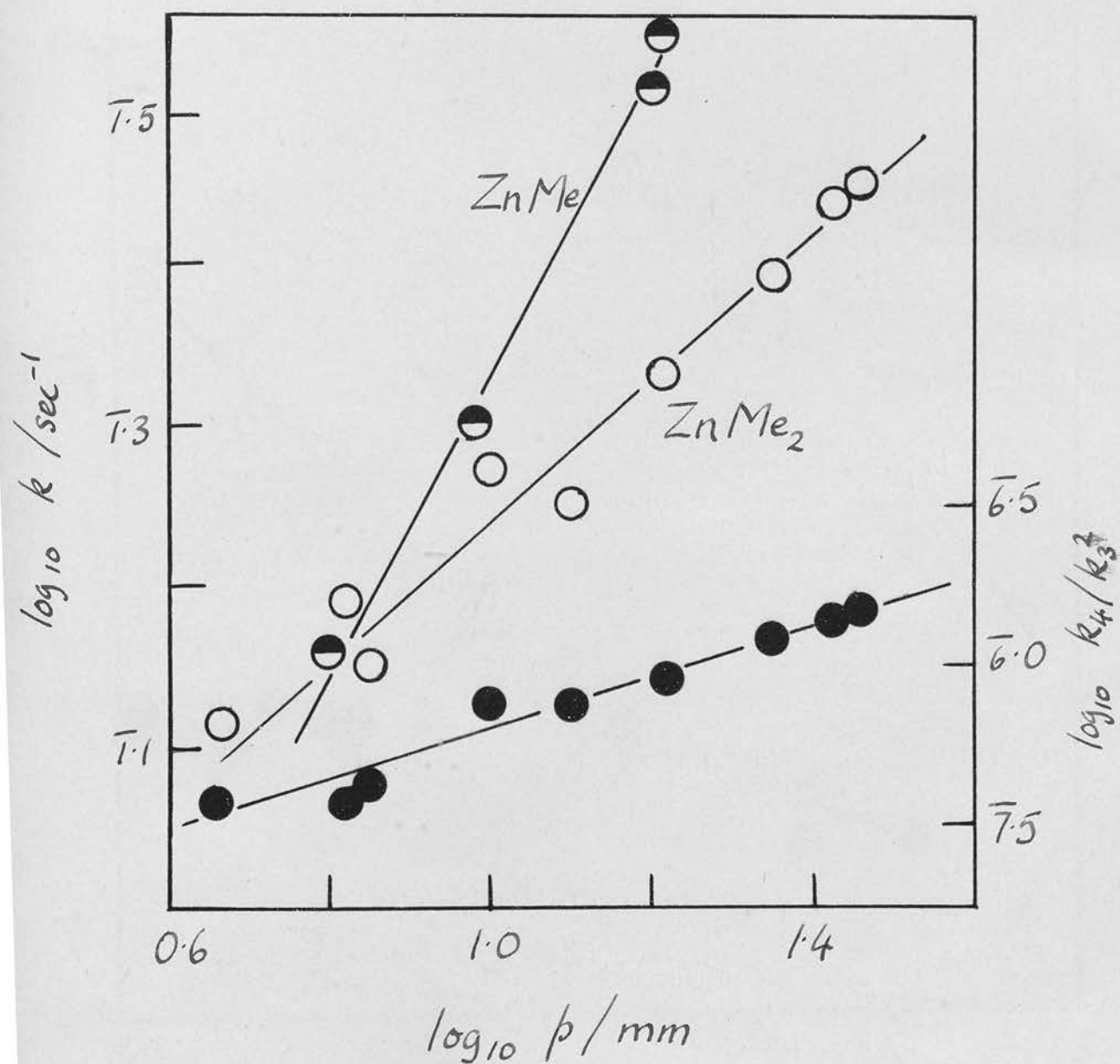


Fig 1.

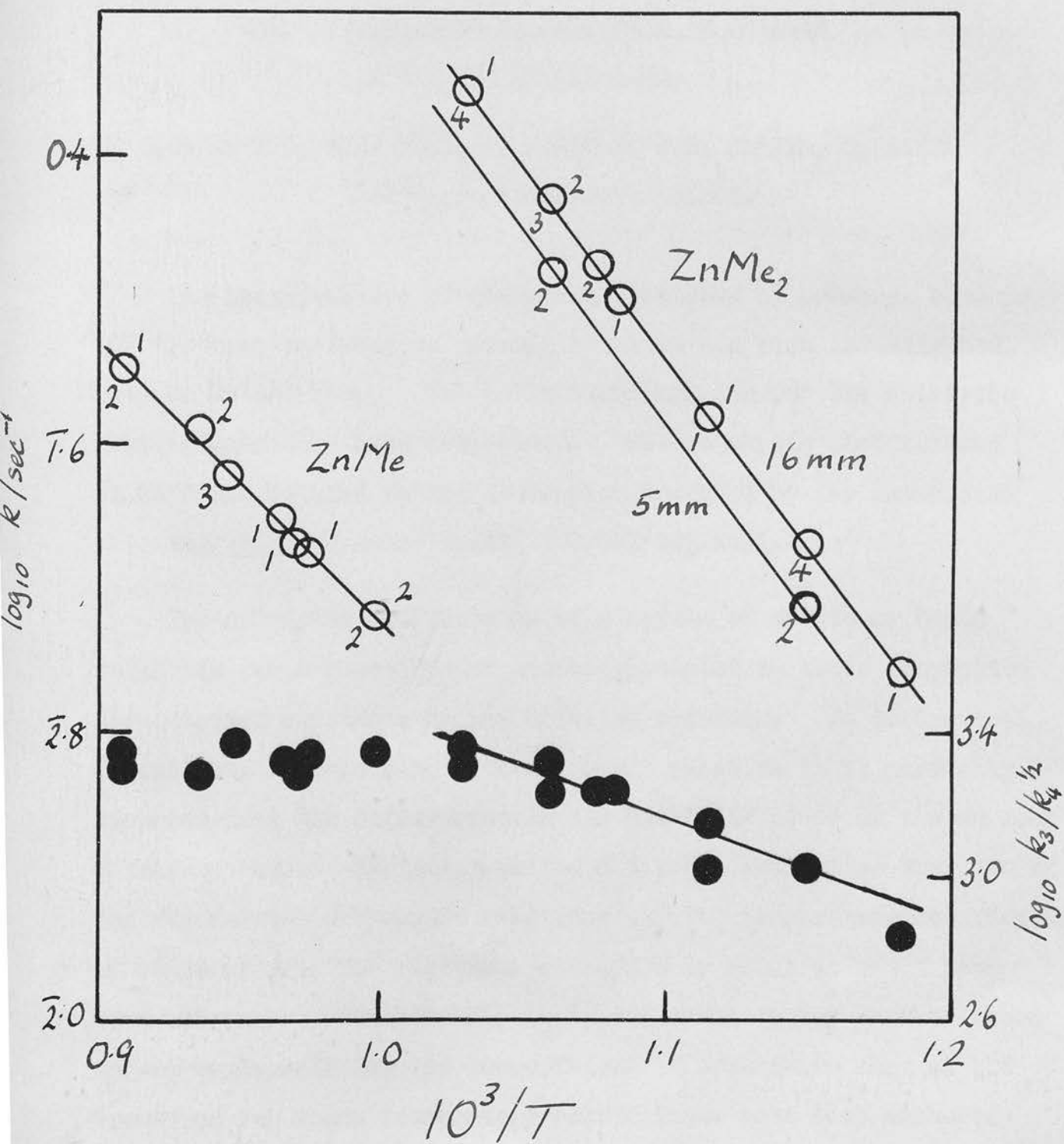


Fig 2.

Proofs to A.F. Trotman-Dickenson,
Chemistry Department,
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Edinburgh 9.

The Decomposition of Nitramide in Anisole

catalysed by Anilines.

by G.C. FETTES, J.A. KERR, A. McCLURE, J.S. SLATER, C. STEEL
AND A.F. TROTMAN-DICKENSON.

The decomposition of nitramide catalysed by primary, secondary and tertiary anilines in anisole solution has been investigated between 7° and 55°C. The activation energies for the catalytic coefficients have been determined. The catalytic coefficients at 25°C are related to the activation energies by the expression

$$\log_{10} k_c(25^\circ) / \text{mole}^{-1} \text{kg} \text{min}^{-1} = 23.2 - 1.63E / \text{kcal.mole}^{-1}$$

The catalytic coefficients of a series of acidic or basic catalysts for a reaction are normally related to their respective dissociation constants by the Brønsted relation. In theoretical discussions of this kind of free energy relation it is generally supposed that the differences in the catalytic power of the various catalysts can be attributed to the different activation energies of the fundamental protolytic reactions¹. The temperature coefficients of comparatively few reactions catalysed by acids or bases have been measured. Consequently it is difficult to say whether there is any real basis for the supposition. Furthermore most of the reactions for which temperature coefficients have been measured have been studied in aqueous solution. It is known that ionic

processes in aqueous solution frequently do not conform to the simplest types of energy relationship. Accordingly it is not surprising that the results obtained with aqueous solutions do not often yield simple relations between the catalytic coefficients and activation energy.

This work was undertaken to obtain results in a solvent which does not readily form hydrogen bonds. The decomposition of nitramide was chosen because it has been very fully investigated and may easily be followed¹. Anisole is a convenient solvent which may easily be sufficiently purified and in which a considerable amount of work has been done. The substituted anilines were chosen as catalysts because they have also been fairly fully studied and are readily available¹⁻⁴.

EXPERIMENTAL.

Materials. The anisole was dried (CaCl_2) and fractionated on an 18" column packed with glass helices. Several batches were purified; all behaved similarly. The anilines were distilled over potassium hydroxide pellets under reduced pressure and stored in sealed containers. The nitramide was prepared by the method of Marlies, Lamer and Greenspan⁵ and stored in a refrigerator as a solution in anisole.

Apparatus and Procedure. The runs were carried out in reaction

vessels similar to those of Bell and Caldin³. The faster runs were carried out in vessels with taps, the slower runs were carried out in sealed vessels. The vessels were placed in a glass-fronted thermostat which could be maintained to $\pm 0.02^\circ\text{C}$ and were agitated by percussion. Reaction mixtures were made up by weight. First a convenient quantity of catalyst (or catalyst solution for the stronger bases) was weighed in a weighing bottle. Sufficient anisole to make approximately 2g. of mixture was then added. Finally 2c.c. of nitramide solution was added immediately before the mixture was introduced into the reaction vessel.

The runs were followed by observing the increase in the pressure of the evolved gas. First order plots were then drawn, based on the pressure of gas after complete reaction. In the slowest runs the reaction vessels were placed in a warm bath to bring the reaction to completion overnight. The rate constants were deduced from the observations taken during the first two half-lives of the reactions, after which some of the plots tailed off. The catalytic coefficients of the bases were found to be a function of the concentration of the solutions. The extrapolations devised by Bell and Trotman-Dickenson³ were used to obtain the true coefficients.

RESULTS.

The results of the kinetic measurements are shown on the

Arrhenius plots (Fig. 1a and 1b) which show the catalytic coefficients from the individual runs and the extrapolations employed. The results are summarized in Table I. Generally the results agree very well with those of Bell and Trotman-Dickenson³ and Bell and Caldin⁴. Those obtained with m-chloraniline are the only exceptions. We can suggest no reason for the discrepancy; the identity of the present material was confirmed by measurement of its refractive index and of the melting point of its acetyl derivative. The accuracy of the determination of the activation energies cannot be readily assessed because of the need for the extrapolation. An error of $\pm 0.3 \text{ kcal.mole}^{-1}$ may reasonably be assigned.

DISCUSSION.

The activation energies of the catalytic coefficient are plotted against the catalytic coefficient of the various bases at 25°C in Fig. 2. All except o-chloraniline lie on a straight line given by $\log_{10} k_c(25^\circ\text{C}) = 23.2 - 1.63E$. The deviation of the ortho-substituted compound is not surprising; many free energy relationships break down for ortho-compounds. The slope of the line in Fig. 2 differs markedly from that which would be obtained (shown dotted) if all the differences between the catalytic coefficients could be attributed to variations in activation energy. The line representing the variation of $\log_{10} k_c$ with E deviates from the

'theoretical' slope, which corresponds to a constant value of \underline{A} , for many series of reactions. Usually the slope is too great, that is systematic changes in \underline{A} compensate for the variations in \underline{E} . In the present reaction the reverse occurs; \underline{A} is not constant; it varies so as to reinforce the changes in \underline{E} .

The fact that the activation energies of the primary, secondary and tertiary bases (with the exception of o-chloraniline) obey the same relationship lends some support to the interpretation of the basic strength of amines, as measured in aqueous solutions, which has been suggested by Bell and Trotman-Dickenson^{2,6}.

Table I.

Base	ke Catalytic coefficients, $10^3 \text{ kg/mole}^{-1} \text{ kg} \frac{\text{m}^3}{\text{m}^3} \text{ sec}^{-1}$			$\log_{10} A$	$\frac{E}{\text{kcal mole}^{-1}}$	
Diethyl-p-toluidine	480(7.6)	2295(25.0)	6760(39.6)	17340(54.1)	9.43	13.9
Dimethyl-p-toluidine	105(7.6)	599(25.0)	1730(39.6)	4875(54.1)	9.22	14.5
Dimethyl aniline	31(8.6)	150(25.0)	425(40.0)	1230(54.1)	8.81	14.8
Methyl aniline	4.28(7.7)	27.6 (25.0)	72.3 (40.0)	242(54.1)	8.17	15.0
Aniline	-	8.07(25.0)	30.0 (40.0)	80.0 (54.0)	8.21	15.5
m-Chloroaniline	-	.85(25.0)	2.90(39.6)	9.5 (54.1)	7.44	16.1
O-Chloroaniline	-	.20(25.0)	1.43(40.0)	3.80(54.1)	5.87	14.1

CAPTIONS

Fig. 1a and 1b Arrhenius plots for the decomposition of nitramide in anisole catalysed by anilines. The individual points and the extrapolations are shown. Open circles: this work, filled circles: Bell and Trotman-Dickenson³; squares: Bell and Caldin². All concentrations in mole kg⁻¹. Except where the scale is marked b when the second method of extrapolation was used, the concentration scale on the abscissae is for 1/*N*^b corresponding to the first method of extrapolation.

Fig. 2. The relation between activation energies and catalytic coefficients for the aniline-catalysed decomposition of nitramide.

1. Bell, Acid Base Catalysis, Oxford, 1941.
2. Bell and Caldin, Trans. Faraday Soc., 1951, 47, 50.
3. Bell and Trotman-Dickenson, J., 1949, 1288.
4. Bell and Wilson, Trans. Faraday Soc., 1950, 46, 407.
5. Marlies, Lamer and Greenspan, Inorganic Syntheses.
6. Trotman-Dickenson, J., 1949, 1293.

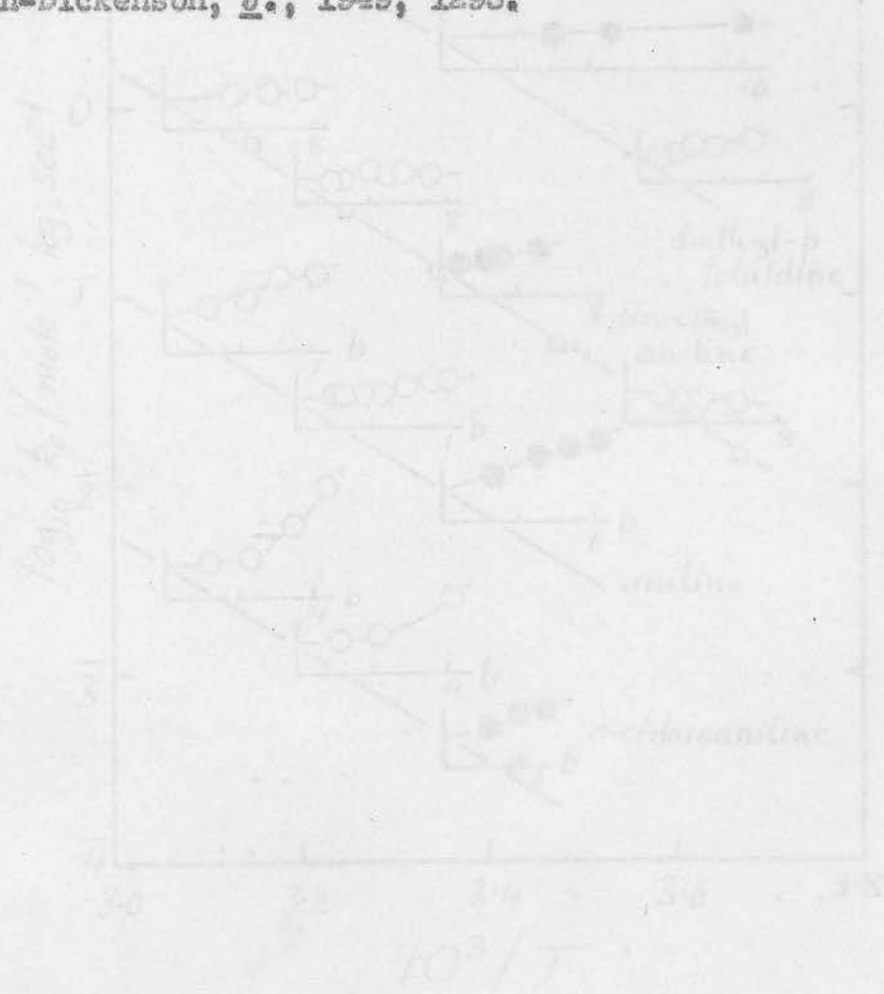


Fig 1

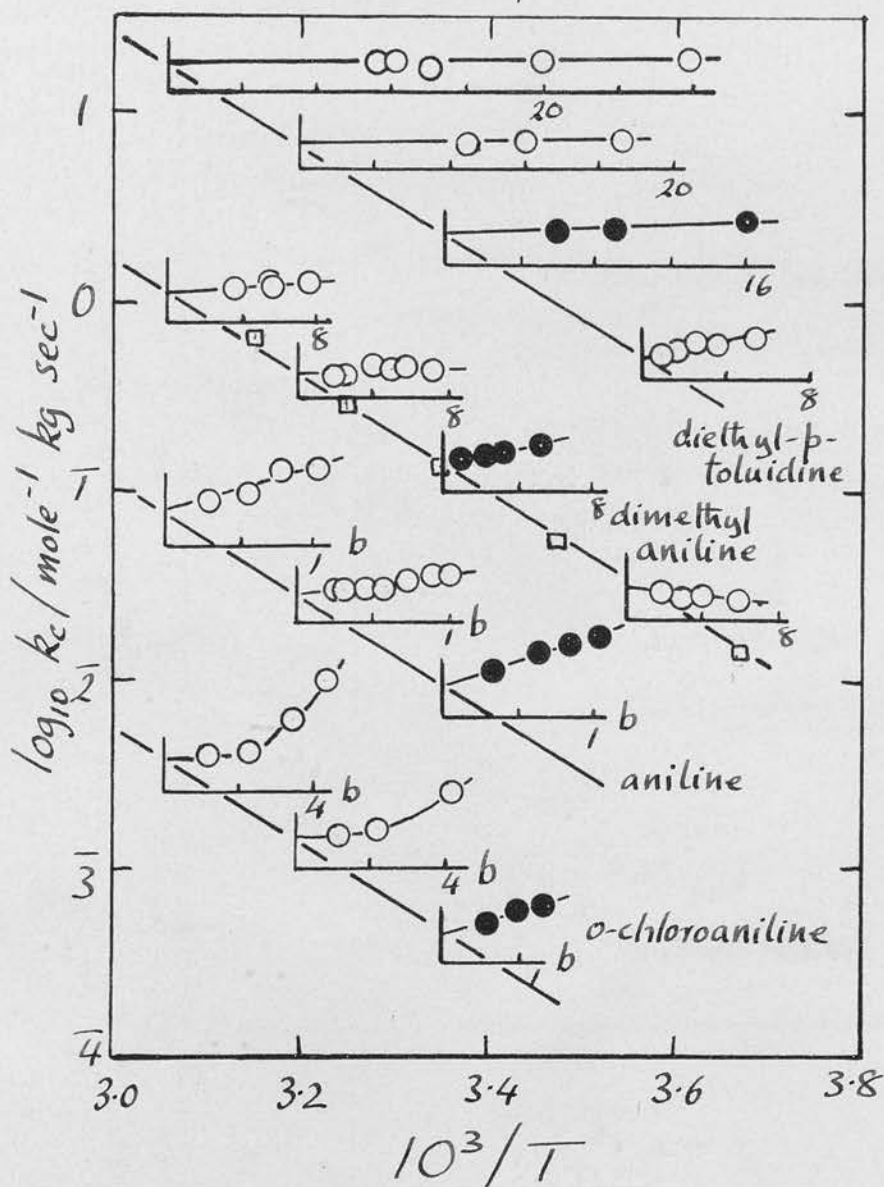


Fig 1

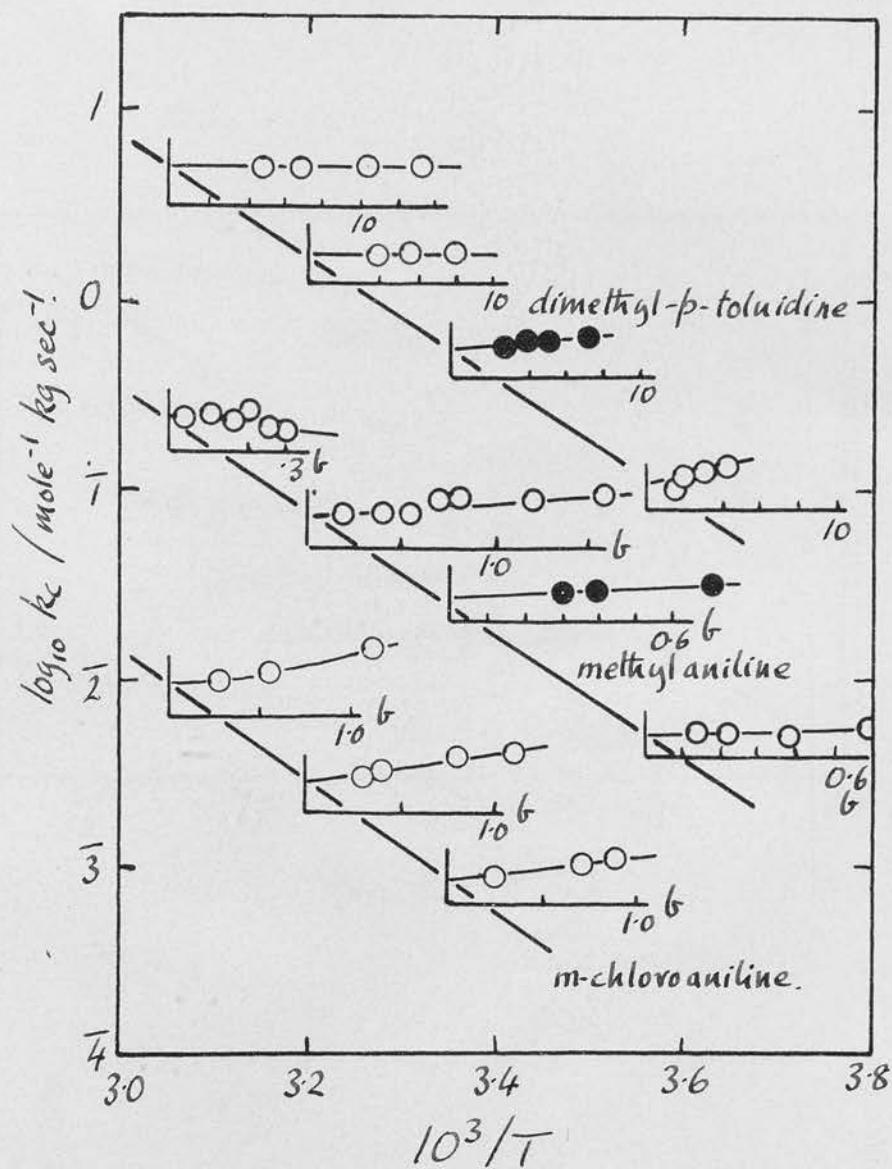


Fig 1

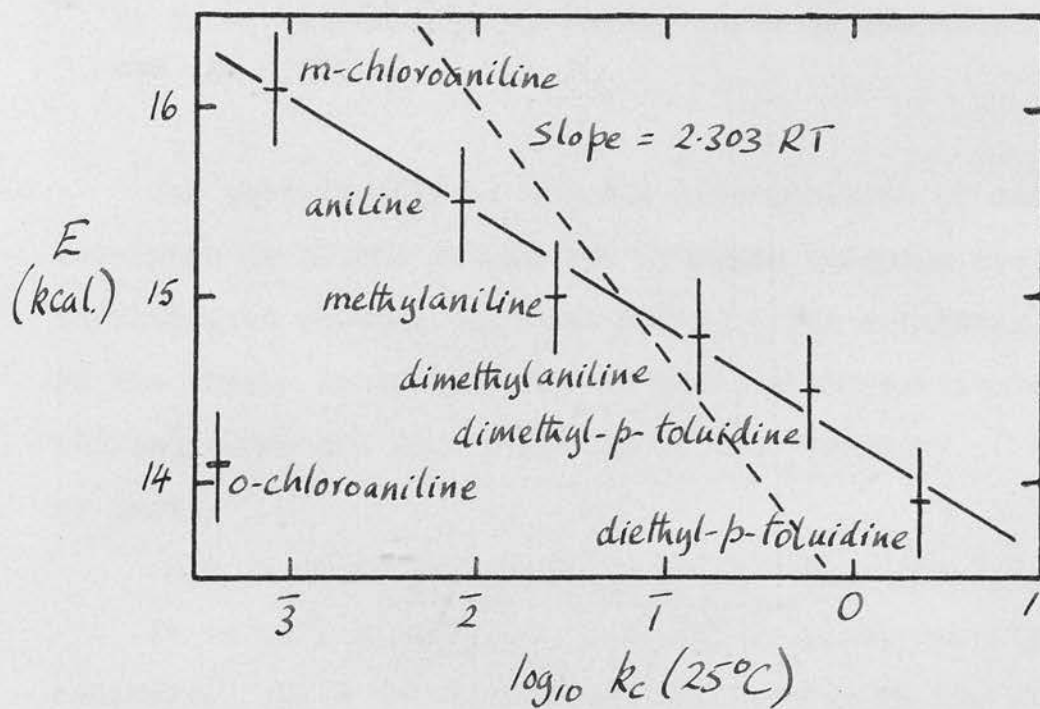


Fig 2.

Proofs to: A. F. Trotman-Dickenson, Department of Chemistry,
The University, West Mains Road, Edinburgh, 9.

THE PHOTODECOMPOSITION OF ACETALDEHYDE

CATALYSED By THIOLS.

By R. N. BIRRELL, R. F. SMITH, A.F. TROTMAN-DICKENSON
and H. WILKIE.

The photo-initiated thermal decomposition of acetaldehyde catalysed by alkane thiols and hydrogen sulphide has been investigated between 168° and 396°C. The catalytic effect of the thiols is independent of their concentration over a limited range and is a function of the structure of the thiol so that



It is well established that thiols react readily with free radicals. This property finds application in the use of thiols as chain transfer agents in free radical polymerisation. However, very few kinetic studies of reactions involving thiols and thiyl radicals have been reported. The only comprehensive study of thiol catalysis appears to be that of Barrett and Waters. They investigated the catalysis of the chain decarboxylation of several saturated aliphatic aldehydes by alkane thiols, in the liquid phase. The reaction chains were initiated by the thermal decomposition of dimethyl- α '-azo-iso-

butyrate and α' -azo-iso-butyronitrile. They supposed that the catalysis could be attributed to the supercession of the reaction (1')



by the faster cycle (2', 3')



The predominant chain carrying step in the high temperature photo-initiated decomposition of acetaldehyde in the vapour phase is almost certainly (1)²



It appeared to be of interest to study the effect of adding thiols to the system, to see if (1) would be superseded by the reactions equivalent to (2') and (3'). Experiments were therefore carried out with a number of thiols over a range of temperature. It was hoped that information would be obtained on the effect of structure on the reactivity of the thiols and on the relative rate constants of the reactions.

EXPERIMENTAL.

Materials: The acetaldehyde was prepared by the distillation of paraldehyde containing a little sulphuric acid: it was thoroughly degassed before use, and stored as a gas in a blackened bulb. The hydrogen sulphide was generated in a Kipp's apparatus, dried and degassed before use. The thiols

were commercial samples; they were thoroughly degassed.

Apparatus: The reactions were carried out in two very similar Pyrex reaction vessels, of about 200 c.c. each, placed side by side in an electric furnace with a quartz window. They were illuminated by the full light from a medium pressure mercury arc which was allowed to warm up for at least twenty minutes before a run. The lamp was run continuously throughout a series of runs. Some runs with methane thiol were carried out with twin quartz cells. One of the cells was connected to a mercury manometer. The other was connected to a di-n-butyl phthalate manometer for the measurement of the small quantities of thiol and to a Bourdon gauge with optical lever for the measurement of the total pressure. It was found that when the cells were filled to the same pressure of ^{pure}acetaldehyde, the difference in the rates of photolysis was not significant. The cells, manometers and storage bulbs were attached to a conventional vacuum line.

Procedure: A convenient pressure of thiol was admitted to one of the cells. Identical partial pressures of acetaldehyde were then admitted to both cells. The dead space was small, so that the measured pressures of reactants corresponded closely to the composition of the mixtures in the cells. After a lapse of a few minutes to allow the gases to come up to temperature, light was admitted to the cells. The change in total pressure in each

was then followed on a manometer. Measurements of the total pressures were made at conveniently spaced intervals.

RESULTS and DISCUSSION.

It has been established by many workers that the products of the photo-initiated thermal decomposition of acetaldehyde are almost exclusively methane and carbon monoxide. In confirmation of this we found that the pressure in the vessel containing pure acetaldehyde approximately doubled when the run was carried to completion. The ultimate pressure increase in the vessel containing the thiol was always about 10% less than the initial partial pressure of acetaldehyde.

The catalytic effect of the thiol was determined from observations taken at the beginning of the reaction. The time taken for an increase in pressure equal to one-fifth of the initial pressure of acetaldehyde was measured for the catalysed and uncatalysed system. It was found that substantially the same ratio was obtained if the initial slopes of the decomposition curves were measured or alternatively the ratios of the times taken to reach some other small degree of decomposition.

Most work was carried out with methane thiol as the catalyst. It was found that at a given temperature and pressure of acetaldehyde the catalytic effect of the thiol increased as its concentration was increased. Then the catalytic effect remained constant over a considerable range of concentration. Finally,

when the thiol concentration was about three-quarters of the acetaldehyde concentration, the ratio increased at low light intensities. The variation of the ratio with concentration is shown in Figure 1. All the points shown were obtained with an initial pressure of 10 cm. of acetaldehyde and with the same incident light intensity. It was found that in the concentration range represented by the flat portion of the curve no alteration in the ratio was brought about by doubling the aldehyde concentration or by varying the incident light intensity by a factor of four. The values of the constant rate ratios were determined at five temperatures between 189° and 396°C. The values obtained have been plotted on the Arrhenius plot, Figure 2.

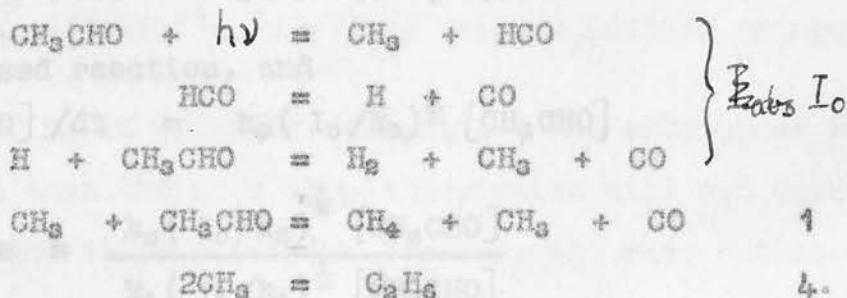
Similar results were obtained from the experiments in quartz reaction vessels, though the rate ratios were always somewhat higher. It is likely that some reaction chains were initiated by the photolysis of the thiol by the unfiltered light from the mercury arc.

Similar experiments were carried out with each of the other thiols. Again it was found that for hydrogen sulphide and ethane thiol, the rate ratio increased with increasing thiol concentration until it reached a constant value, Figure 1. With ethane thiol as the catalyst the rate ratios were independent of a variation in absorbed light intensity of a factor of nine. The interpretation of the results with hydrogen sulphide is more

uncertain. A slight induction period was evident at low light intensities and high concentrations of the sulphide. The rate ratios corresponding to the plateau are plotted against temperature for both catalysts in Fig. 2.

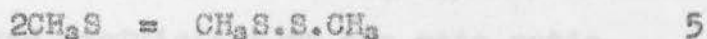
The catalytic behaviour of propane-2-thiol and 2-methyl-propane-2-thiol is shown in Figure 1. A constant rate ratio is never maintained over any considerable range of concentration, though the rate ratios are independent of a variation of light intensity of a factor of four. For purposes of comparison the maximum rate ratios for these catalysts are plotted against temperature in Figure 2. At temperatures above 300°C. a small quantity of 2-methyl-propane-2-thiol reduced the rate of the decomposition of acetaldehyde to negligible proportions. Propane-2-thiol behaved in the same manner at temperatures about 40°C. higher. There was no evidence that this inhibition was caused by products of the thermal decomposition of the thiols.

The mechanism of the photo-initiated thermal decomposition of acetaldehyde has often been written as:



It is now known that this is not a complete description of the reaction system, but it certainly represents the principal

reactions correctly. A mechanism similar to that proposed by Bassett and Waters is adequate to cover the facts of the catalysis by methane thiol. The steps immediately consequent upon the absorption of light are followed by:



Disulphides have been found in the products of thiol catalysed reactions at low temperatures, which lends support to reaction 5.

It is a necessary feature of the mechanism that k_2 , the rate constant for reaction 2 should be very much greater than k_1 or k_3 . Unpublished results of Mr J. A. Kerr in this laboratory indicate that at low temperatures k_2 is at least fifty times k_1 .

Solution of the steady state equations yields (neglecting the decomposition in the initiating step)

$$-d [\text{CH}_3\text{CHO}] / dt = k_1 (I_0/k_4)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]$$

for the uncatalysed reaction, and

$$-d [\text{CH}_3\text{CHO}] / dt = k_3 (I_0/k_5)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]$$

$$\begin{aligned} \text{Rate ratio} &= \frac{k_3 (I_0/k_5)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]}{k_1 (I_0/k_4)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]} \\ &= (k_3/k_5)^{\frac{1}{2}} / (k_1/k_4)^{\frac{1}{2}} \end{aligned}$$

This equation should apply to the rate ratios in the region where they are independent of the thiol concentration. The rate ratio probably initially increases with thiol concentration because, at the lowest ratios, reaction 2 is not sufficiently faster than reaction 1. Since k_1 and k_4 are known^{3,4}, $k_3/k_5^{1/2}$ may be evaluated. From the temperature coefficient of the rate ratio $E_2 - E_1 - \frac{1}{2}E_5 + \frac{1}{2}E_4$ may be found where the E's are the activation energies of the reactions.

Hence, assuming

$$\log_{10} k_1 / \text{mole}^{-1} \text{cm}^3 \text{sec}^{-1} = 12.1 - (8400/2.303 RT)$$

$$\log_{10} k_4 / \text{mole}^{-1} \text{cm}^3 \text{sec}^{-1} = 13.3$$

we find $E_2 - \frac{1}{2}E_5 = 6800 \text{ cal.}$

Most combinations of small free radicals have very low activation energies and A factors of about $10^{13.3} \text{ mole}^{-1} \text{cm}^3 \text{sec}^{-1}$.

Assuming $\log_{10} k_5 = 13.3$

$$\log_{10} k_3 / \text{mole}^{-1} \text{cm}^3 \text{sec}^{-1} = 11.9 - (6800/2.303 RT)$$

This value of k_3 is probably reliable. The only cause for doubt is the fact that the same simple mechanism will not describe the behaviour of the other thiols. However, the rate ratios with each of the catalysts were independent of their concentration over a detectable range, and also of the absorbed light intensity.

These facts can only be readily interpreted on the assumption that reaction 2' represents the fate of virtually all the alkyl radicals released into the system. Therefore it seems probable that a mechanism substantially parallel to that for methane thiol holds for the other compounds, but that other side reactions must occur. In these circumstances it is impossible to derive rate constants for the elementary reactions. The rate ratio was found to reach its constant value for a lower concentration of methane thiol than for hydrogen sulphide. From such evidence the apparent order of reactivity for methyl radicals with the thiols (reaction 2') may be deduced to be



This order is the opposite to that for the catalytic effect of the thiols ($k_3/k_5^{1/2}$). This is quite understandable. The first reaction would presumably be favoured by a weakening of the S-H bond, whereas the second would be favoured by its strengthening.

We are indebted to the British Petroleum Company for a grant in aid of this work.

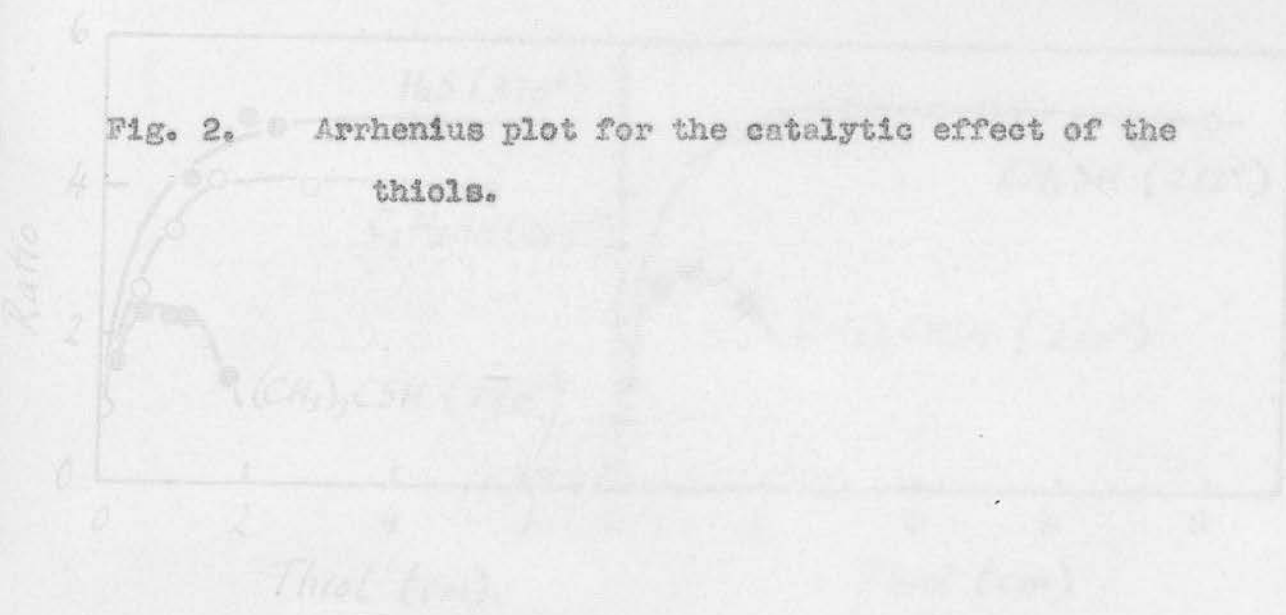
Department of Chemistry,
The University,
Edinburgh.

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Captions.

Fig. 1. Typical variations of catalytic effect with concentration.

Fig. 2. Arrhenius plot for the catalytic effect of the thiols.



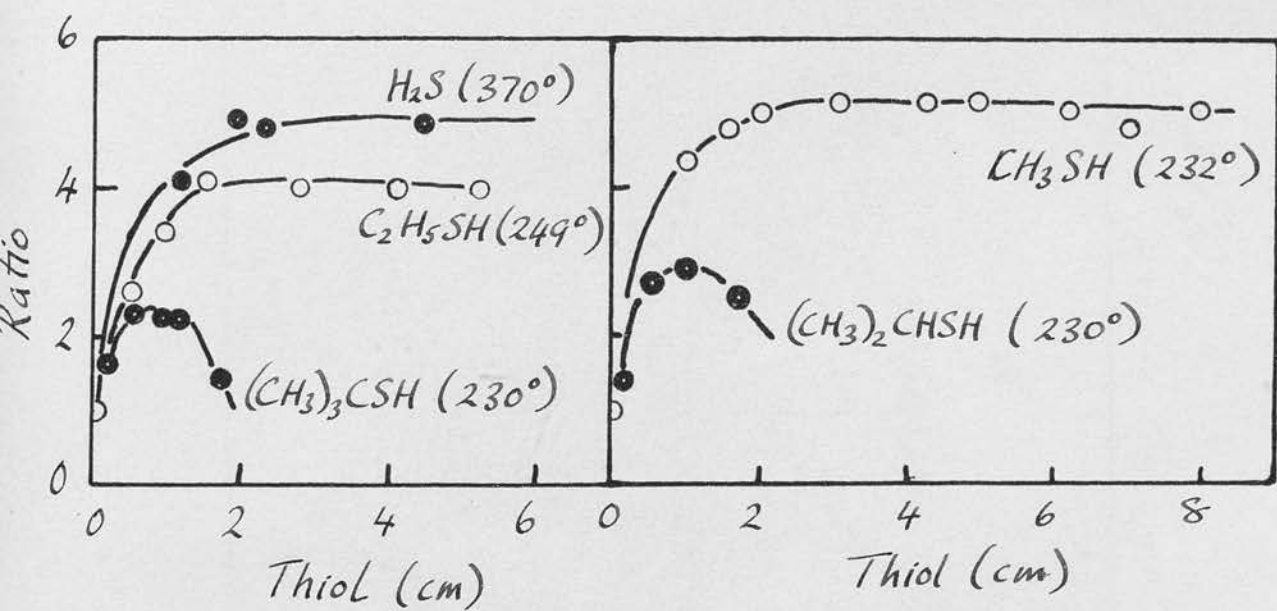


Fig 1

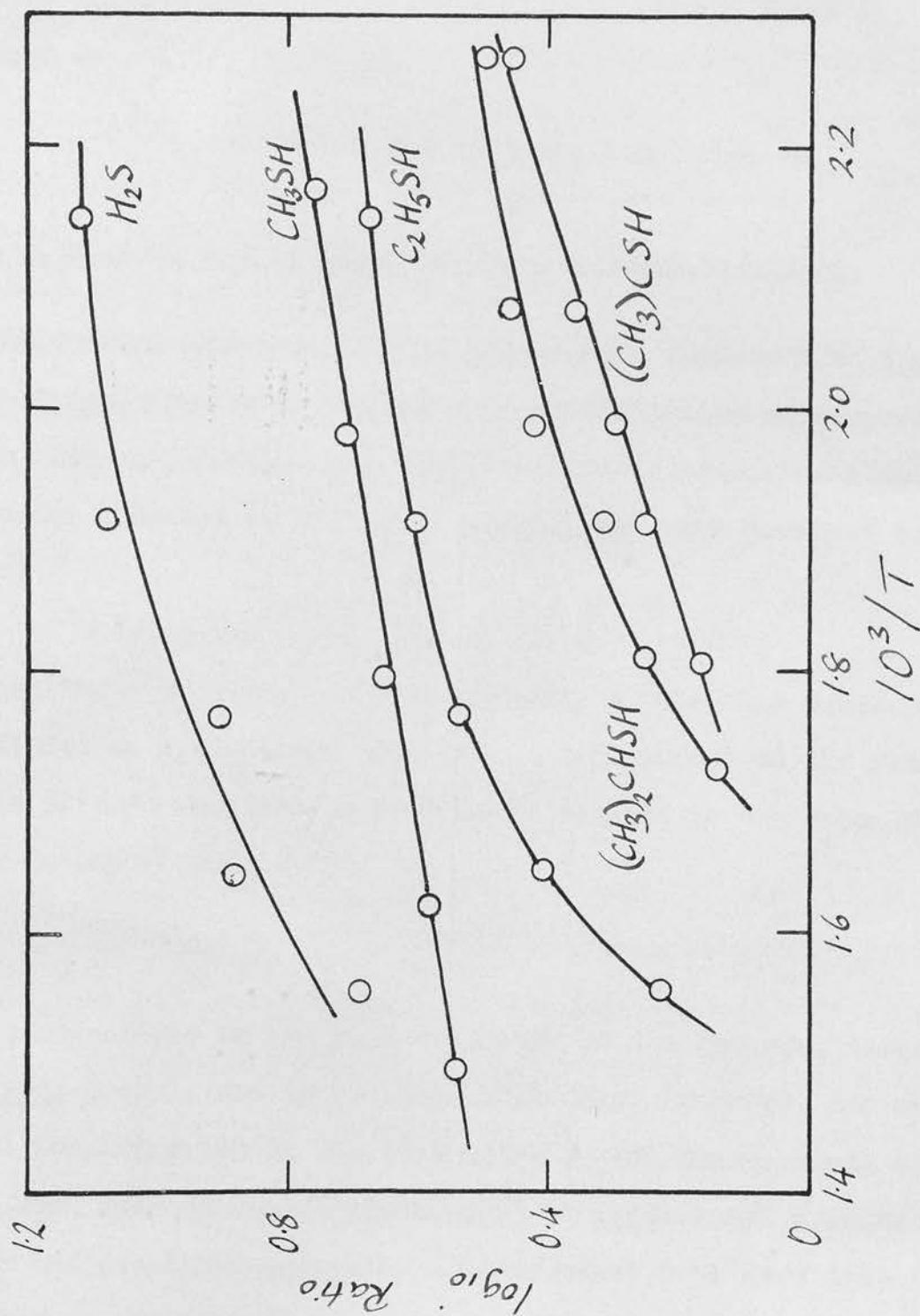


Fig 2.

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West Mains Road,
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The Pyrolysis of tert.-butyl formate.

by E. GORDON, S.J.W. PRICE and A.F. TROTMAN-DICKENSON.

The thermal decomposition of tert.-butyl formate into iso-butene and formic acid has been studied in a static system at temperatures between 230° and 300°C. The decomposition is homogeneous and obeys first-order kinetics in its early stages; the rate constant is given by

$$\log_{10} k / \text{sec}^{-1} = 11.1 - (34\,600 / 2.303RT)$$

The elimination of formic acid is probably a molecular process, as the addition of cyclohexene has a very small effect on the rate. The rate of this reaction is reasonably related to the rates of similar decompositions.

Determinations of the rate constants of the decompositions of ethyl, sec.-propyl, and tert.-butyl chlorides, bromides, and acetates have all been reported in the literature¹. No measurements appear to have been made on the decompositions of tert.-butyl formate although the ethyl and sec.-propyl derivatives have been investigated. The object of the present study was to fill this gap.

EXPERIMENTAL

Materials. - The tert.-butyl formate was specially prepared for use in this investigation by Dr. C. Barkenbus of the University of Kentucky according to the method devised by him². The material was thoroughly degassed and stored in a dry ice bath. It was found that at temperatures appreciably above room temperature and in the absence of a drying agent the liquid rapidly decomposed, apparently into iso-butene and formic acid. The cyclohexene, which was also degassed, was freed from peroxides by shaking with acid ferrous sulphate solution.

Apparatus.- The decomposition was studied in a Pyrex bulb of 385 c.c. capacity attached to a conventional vacuum system by heated tubing with a total dead space of approx. 13 c.c. The unpacked bulb had a surface/volume ratio of 0.9cm^{-1} , when it was packed with fire polished Pyrex tubing the ratio was 3.0cm^{-1} . The bulb was contained in a mercury-vapour jacket, whose temperature could be readily controlled by varying the pressure under which the mercury boiled. The temperature of the jacket was determined^{by} reference to standard tables of the vapour pressure of mercury. The reaction was studied by following the change in pressure in the reaction vessel on a mercury manometer.

Procedure.- Runs were started by admitting a suitable quantity of the formate to the reaction vessel from the storage bulb, in some runs

Percentage decomposition by pressure rise 11.6 10.0 20.0 41.0

Percentage decomposition by iso-butene 7.3 14.4 30.0 29.0

cyclohexane^e was also added. Readings of the pressure in the vessel were then recorded at convenient intervals. Rate constants were determined from first-order plots of the logarithms of the pressure changes against time, based on the assumption that complete reaction corresponded to a doubling of the pressure. The logarithmic plots were strictly linear for the first 70-80% of the reactions at the higher temperatures but thereafter tended to curve slightly. No induction periods were observed.

RESULTS and DISCUSSION.

Tert.-butyl formate was presumed to yield formic acid and iso-butene as the primary products of the decomposition. This presumption is based upon the known ease with which these products are formed in the liquid in the presence of a trace of acid and upon the analogy with the decompositions of the other formates. It was difficult to check this by analysis, because of the rapidity with which the liquid decomposed. Several experiments were done with a trap system in which the formate and formic acid were condensed in a trap cooled in a dry-ice bath and the iso-butene in a trap cooled in liquid oxygen. The iso-butene was then transferred back into the reaction system and its pressure measured. The percentage decomposition based on the formation of iso-butene was then calculated.

The results of a series of runs at 251°C were as follows

Percentage decomposition by pressure rise	11.4	19.0	30.0	41.0
Percentage decomposition by <u>iso</u> -butene	7.9	14.4	30.0	39.0

The method of analysis was not very satisfactory, but there appears to be little doubt as to the nature of the decomposition. Runs which were followed for many half-lives never yielded a pressure greater than twice the initial pressure. This is evidence that the formic acid does not decompose at these low temperatures.

The linearity of the logarithmic plots demonstrated the first-order nature of the decomposition which was confirmed by doing runs with different initial pressures of the formate between 3.8 and 10.3cm. No systematic trend nor variation of the rate constants outside the limit of experimental error was observed.

Fig. I is an Arrhenius plot of the rate constants for the thermal decomposition. The best straight line was calculated by the method of least squares giving equal weight to each run: the points shown in the figure are the mean values obtained at each temperature. The results are best expressed by

$$\log_{10} k / \text{sec.}^{-1} = 11.1 - (34,600 - 900 / 2.303RT)$$

Two facts showed the decomposition to be homogeneous. First, no conditioning of the reaction vessel was needed before reproducible results were obtained. Second, packing the reaction vessel did not affect the rate constants as is shown in Fig. 1 where the mean results obtained in the packed vessel are plotted.

The absence of an induction period and the negligible effect of packing the vessel indicate that the decomposition is molecular

and does not involve free radicals. This was confirmed by adding cyclohexene to the system. The addition of between 20 and 50 per cent of cyclohexene appeared to reduce the rate of decomposition very slightly, but the lowering was of the same order as the experimental scatter. The results obtained with cyclohexene are also shown in Fig. 1.

The activation energy of this decomposition is markedly lower than those for the decomposition of ethyl formate ($44.1 \text{ kcal. mole}^{-1}$) and of sec.-propyl ($44.0 \text{ kcal. mole}^{-1}$)³. However it is often found to be more enlightening to compare the variation of the rate constants of a series of reactions rather than their A factors and activation energies. Such a comparison is made for several series of ethyl, sec.-propyl and tert.-butyl esters in Fig. 2. All of these decompositions are thought to be molecular. The rate constants are corrected to 380°C and are expressed in terms of the rate constant of the ethyl ester which has been assigned the value unity. In the figure the logarithms of the rate constants are plotted against the logarithms of the rate constants for the decomposition of the ethyl, sec.-propyl and tert.-butyl bromides. The line labelled 'hydrides' represents the rate constants for the decompositions of ethyl bromide, n-propyl bromide and iso-butyl bromide. It is evident that the same factors control the rates of each series of reactions.

We are greatly indebted to Dr. C. Barkenbus for the sample of the tert.-butyl formate and to the British Petroleum Company for a grant.

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Fig. 2. The relation between the rates of the molecular decompositions of various ethyl, sec.-propyl and tert.-butyl derivatives.

CAPTIONS.

Fig. 1. Arrhenius plot for the thermal decomposition of tert.-butyl formate.

O Unpacked vessel

⊙ Packed vessel

+ Unpacked vessel with the addition of cyclohexene.

The figures by the circles indicate the number of runs averaged to obtain each point.

Fig. 2. The relation between the rates of the molecular decompositions of various ethyl, sec.-propyl and tert.-butyl derivatives.

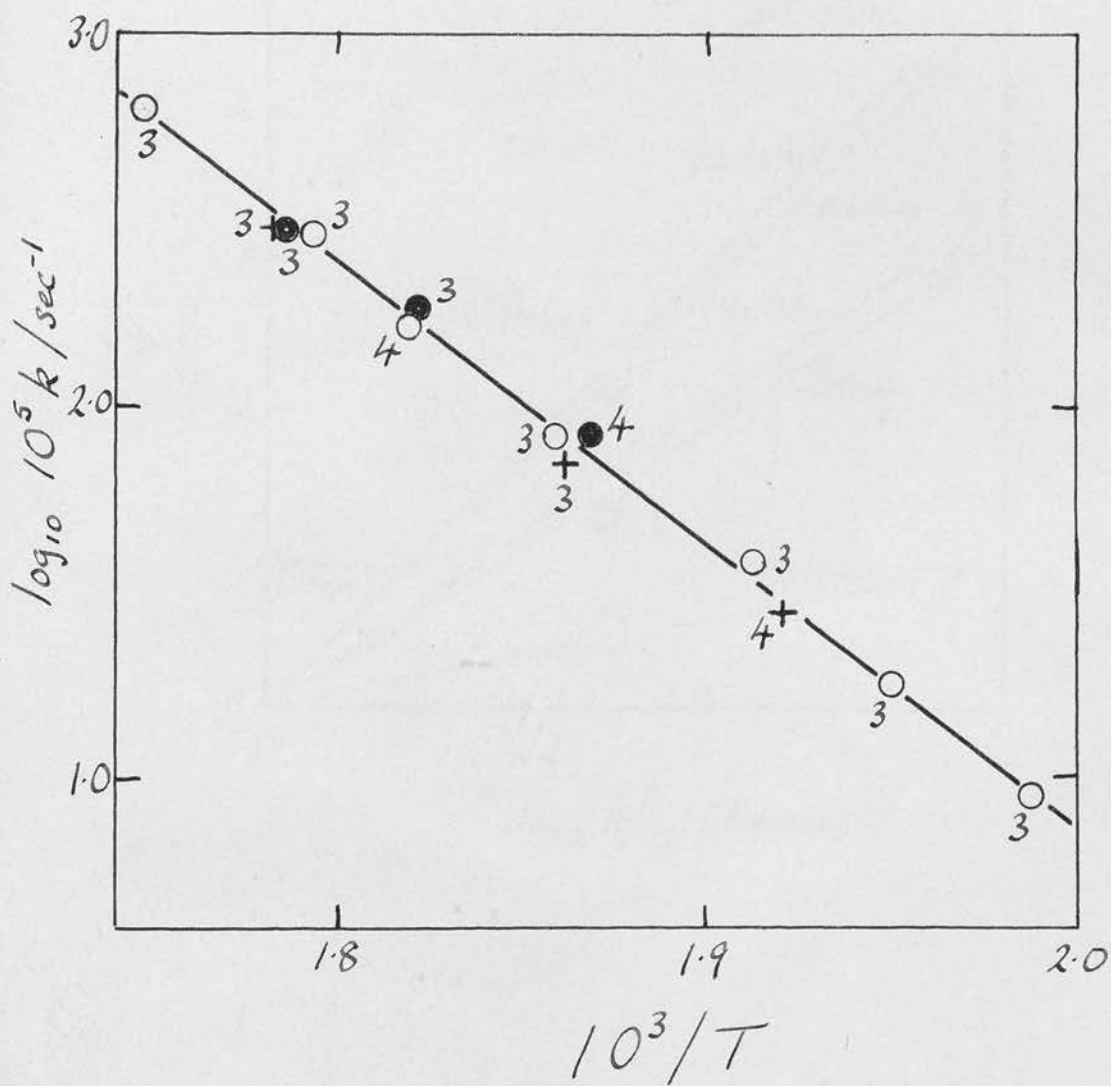


Fig 1.

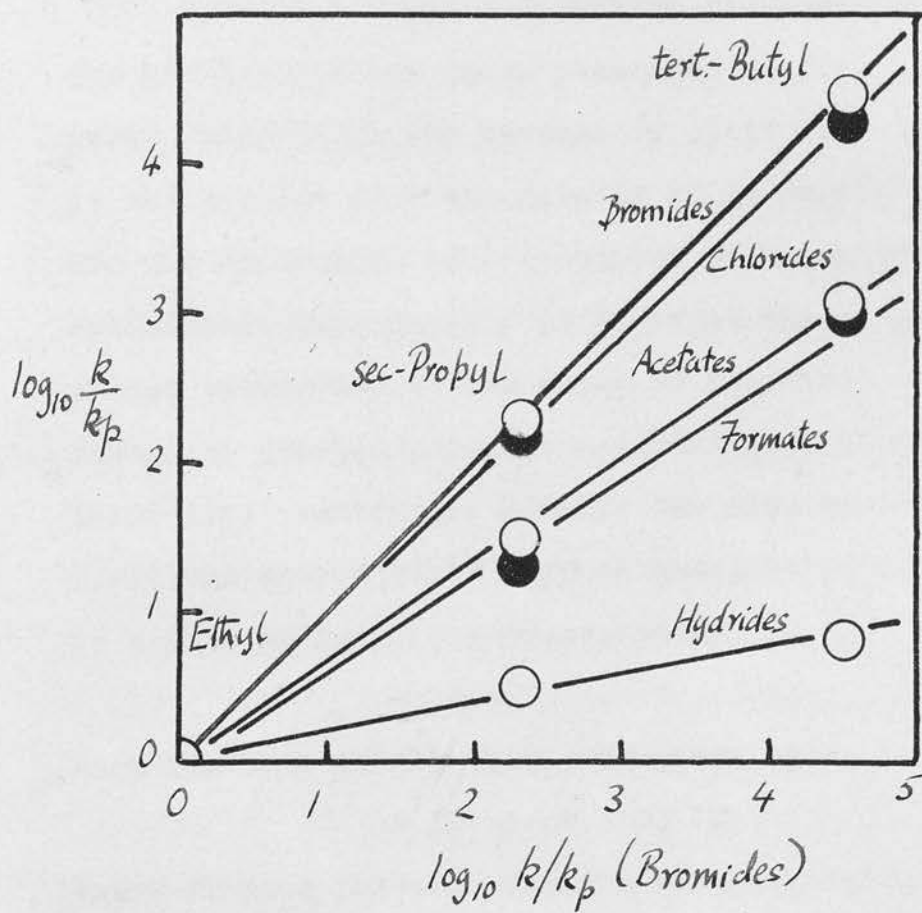
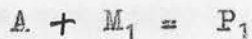


Fig 2

THE STUDY OF RADICAL REACTIONS BY COMPETITIVE METHODS

by J.H.Knox and A.F.Trotman-Dickenson

The bimolecular gas phase reactions of free radicals merit study primarily because of their formal simplicity. At the present time the methods of measuring rate constants are far in advance of the methods by which they may be calculated. Consequently it is right that much effort should be devoted to the study of reactions that are simple enough to provide possible material for the evaluation of theoretical estimates. Ideally the rate constants of these reactions should be determined absolutely. If the reaction of a free radical is represented by



then its rate constant, k_1 , is given by

$$R_1 = k_1 (A) (M_1)$$

where R_1 is a suitable measure of the progress of the reaction. The rate constant may be determined over a range of temperature and its temperature dependence may be expressed as

$$k_1 = A_1 \exp (-E_1/RT).$$

The greatest success in the calculation of rate constants has from attempts that have been made to predict the A factors and the activation energies independently. Calculations based upon the transition state theory yield A factors which are of the correct order of magnitude. Activation energies may also be understood in terms of the

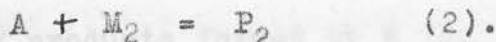
transition state theory but they cannot be calculated from first principles with useful accuracy.

The evaluation of k_1 involves the determination of three quantities:

- (a) The concentration of the normal reactant M_1 .
- (b) The concentration of the free radical A.
- (c) The progress of the reaction, R_1 .

(a) The concentration of M_1 in the reaction mixture may readily be measured and may be maintained effectively constant throughout the reaction if the percentage conversion is kept low.

(b) The concentration of the free radical A cannot in general be directly determined. Usually it can only be found by the measurement of a concurrent reaction whose rate constant is known or may reasonably be assumed. This is the essence of the competitive method. In the present paper we shall only be concerned with cases in which the molecularity of the standard reaction with respect to A is the same as that of the reaction whose rate constant is to be measured, and is of the same kind. As an example we may consider the two reactions:



If these two reactions occur simultaneously in a reaction vessel, then

$$R_1 = k_1(A)(M_1) \quad \text{and} \quad R_2 = k_2(A)(M_2)$$

hence

$$\frac{k_1}{k_2} = \frac{R_1}{R_2} \frac{(M_2)}{(M_1)}$$

Thus the ratio of the rate constants may be determined without measuring (A). If k_1 is known then k_2 may be determined absolutely. It frequently happens that this is the most convenient way of determining a series of rate constants, k_2 , even for systems in which it might be possible to apply the methods by which k_1 was absolutely determined. The competitive method has the additional advantage that it is unnecessary to maintain the concentration of constant throughout the duration of a run.

(c) The problem is thus reduced to one of measuring the rates of the reactions, R_1 and R_2 . Together with our colleagues we have obtained reasonably satisfactory solutions in three different ways:

(1) When the reactions to be studied are hydrogen abstraction reactions, then distinctive products may be obtained for measurement if one of the substrates is deuterated. This approach has been used in the study of the reactions of trideuteromethyl¹ and trifluoromethyl² radicals.

(2) The amounts of M_1 and M_2 consumed may be determined. This approach has been used in the study of the reactions of chlorine atoms³.

(3) The amounts of products formed by the released substrate radical may be determined. This approach has also been used in the study of the reactions of chlorine atoms⁴ and adapted to the study of the reactions of methylene.

1. The Reactions of Trideuteromethyl Radicals¹. The most

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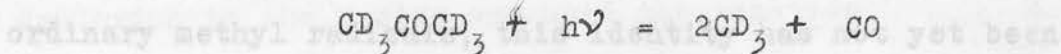
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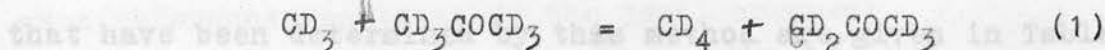
(3) The amounts of products formed by the released substrate radical may be determined. This approach has also been used in the study of the reactions of chlorine atoms⁴ and adapted to the study of the reactions of methylene.

1. The Reactions of Trideuteromethyl Radicals¹. The most

convenient source of trideuteromethyl radicals is the photolysis of hexadeuteroacetone. At temperatures above 120°C the photolysis may satisfactorily be represented by



The methyl radicals then react as follows:



Kistiakowsky and Roberts⁵ have studied this system using the method of intermittent illumination and hence found that the absolute value of the rate constant of reaction (1) is given by

$$\log_{10} k_1 / \text{mole}^{-1} \text{cm}^3 \text{sec}^{-1} = 11.6 - (10300/2.3RT)$$

In the presence of a hydrogen-containing compound the following additional reaction occurs



Following the argument given above, we have

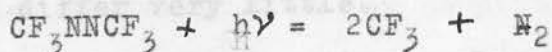
$$k_2/k_1 = (\text{R}_{\text{CD}_3\text{H}}/\text{R}_{\text{CD}_4}) ([\text{CD}_3\text{COCOD}_3]/[\text{RH}]).$$

The ratio of $\text{CD}_3\text{H} : \text{CD}_4$ may readily be determined by the analysis of the non-condensable fraction of the products with a mass-spectrometer. The intense parent peaks of the two methane ions at mass 19 and 20 are free from interference from the ions of the other molecules that may be present. A particular virtue of this method is that methane produced by side reactions such as the decomposition of radicals will not be deuterated and will not interfere. The absence of the need to analyse for ethane is also convenient if the reactions of ethylene and other low -

boiling compounds are to be studied. It is usually assumed that the rate constants of the reactions of deuteromethyl radicals are very similar to those of the reactions of ordinary methyl radicals; this identity has not yet been experimentally established. Examples of some rate constants that have been determined by this method are given in Table 1. The method is particularly suitable for the measurement of the rate constants for reactions with a series of very similar compounds such as the alkenes. The relative values of the rate constants are probably very accurate. Taken in conjunction with results that have been obtained with the alkanes, these figures show that the high reactivity of the higher alkenes is associated with the presence of the α -methylenic hydrogen atoms. The reactivity of these hydrogen atoms varies in the order

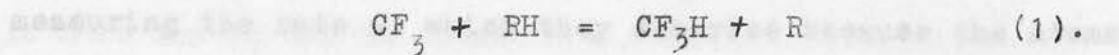
primary < secondary < tertiary.

The reactions of Trifluoromethyl Radicals.² There are two reasonably satisfactory sources of trifluoromethyl radicals, hexafluoroacetone and hexafluoroazomethane. Although hexafluoroacetone is now known to offer considerable advantages we used hexafluoroazomethane because it is readily prepared from iodine penta fluoride and iodine cyanide. When it is photolysed the following reactions occur:

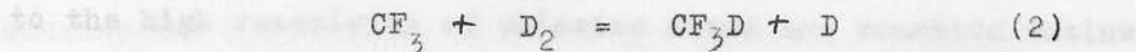


There is also some addition of trifluoromethyl radicals to the double bond, but no abstraction of fluorine atoms to yield CF_4 takes place. In the presence of a hydrogen-

containing compounds CF_3H is formed by the reaction



In order to study a series of such abstractions we added deuterium to the system and used the reaction



as a reference reaction. By the usual argument

$$k_1/k_2 = (R_{\text{CF}_3\text{H}}/R_{\text{CF}_3\text{D}})([\text{D}_2]/[\text{RH}])$$

The ratio $\text{CF}_3\text{H} : \text{CF}_3\text{D}$ may be readily determined with a mass-spectrometer because the ions that are predominantly produced by electron impact are CF_2H^+ and CF_2D^+ . The reference reaction was calibrated against the reaction of trifluoromethyl radicals with ethane; the rate constant for this reaction was determined absolutely by Ayscough, Polanyi and Steacie⁶; it is given by

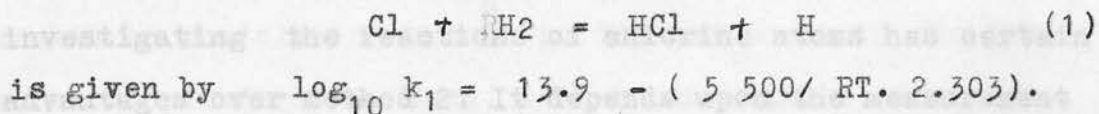
$$\log_{10} k/\text{mole}^{-1}\text{cm}^3\text{sec}^{-1} = 11.7 - (7500/2.3RT).$$

Some results obtained by this method are shown in Table 2. Ayscough and Steacie have obtained results that are in excellent agreement with several of these.

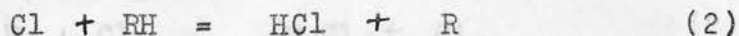
The activation energies given in parentheses are those for the reactions of unsubstituted methyl radicals with the substrates. It can be seen that the reactions of trifluoromethyl radicals have activation energies that are generally lower by 2 to 3 kcal/mole. The A factors of the two sets of reactions differ very little.

2. The Reactions of Chlorine Atoms. Several factors combine to make it impossible to study the reactions of chlorine atoms by the methods that have been used to study the reactions of bromine atoms or of small free radicals. The conc-

entrations of chlorine atoms cannot be determined by measuring the rate at which they dimerize because the atoms are generally produced by dissociation of the element which is present in the system in considerable quantities. Owing to the high reactivity of chlorine atoms the reaction chains in chlorinations are very long and consequently difficult to reproduce. It is therefore impossible to rely simply on the known dissociation constant of the diatomic molecule to estimate the concentration of atoms and hence the rate constants in the way that Kistiakowsky, Van Artsdalen and their coworkers⁷ did when investigating brominations. Fortunately, however, it has been possible, by a series of ingenious arguments,⁸ to show that the rate constant of the reaction



If light is shone on a system containing chlorine, hydrogen and a hydrogen-containing compound RH, the following reaction also occurs



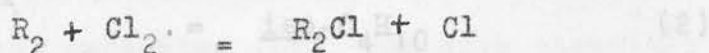
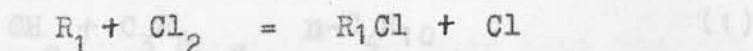
The hydrogen atoms and radicals, R, react with chlorine molecules to yield chlorides and chlorine atoms. It is not convenient to measure the relative rates of the reactions by introducing deuterium into the compound RH, because of the difficulty of measuring the ratio of HCl to DCl.

However the amounts of hydrogen and RH consumed may be measured. Then if the percentage conversion is kept low and the reaction chains are long, we may write

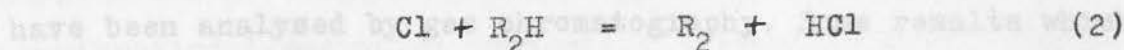
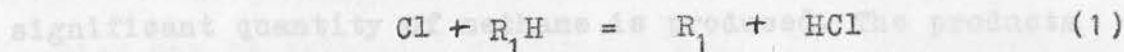
has to $k_1/k_2 = (-R_{H_2}/-R_{RH})([RH]/[H_2])$. In this way k_2 may be found. It is not convenient to compare the reactions of all hydrogen-containing compounds with the hydrogen reaction, because the differences in rates are excessively large. Accordingly one progresses stepwise down a series of compounds. The results that have been obtained in this way are shown in Table 3.

Two points in these results are worthy of note. First the A factors of these reactions closely approach the rate of collision that may be calculated from the kinetic theory of gases. Second the activation energies are extremely low and vary little with the structure of the compounds.

3. The Reactions of Chlorine Atoms. A second method of investigating the reactions of chlorine atoms has certain advantages over method 2. It depends upon the measurement of the amounts of the alkyl chlorides formed by the reaction of the alkyl radicals with chlorine molecules.



These reactions follow inevitably on to reactions:



Accordingly $\frac{k_1}{k_2} = \frac{R_{R_1Cl}}{R_{R_2Cl}} \cdot \frac{[R_2H]}{[R_1H]}$

This method has two considerable advantages. First, the relative rates can be measured more accurately since one

for attack at different positions in the molecules, it is likely that the activation energies themselves are small. This conclusion must be regarded as tentative because the usual factors determining activation energies do not seem to be exerting their normal influence. In particular, attack on the weaker secondary and tertiary C-H bonds requires higher activation energies than attack on the stronger primary bond. Perhaps steric repulsions are, in these cases, more important than bond strengths.

Theoretical Considerations.

As has already been stated it is possible to calculate correctly the order of magnitude of the A factors of many simple free radical reactions. Such calculations can only be made exact if the mechanical properties of the activated complexes are fully known, so that their entropies can be determined. In fact only the translational entropies can be found exactly. Trial calculations show that the rotational entropies of activated complexes with plausible conformations differ very little. Usually these entropies may be estimated within 0.5 e.u. The evaluation of vibrational entropies presents considerable difficulties as there is no empirical rule for estimating vibrational frequencies.

A possible approach is to consider a series of very similar reactions and attempt to calculate their relative

A factors. As has been shown the logarithms of these relative values may be determined experimentally with the same proportional accuracy as absolute A factors. It may be supposed that many of the errors that arise because of incorrect assumptions made about the activated complex will cancel out. This approach would therefore appear to be particularly hopeful because the assumptions chiefly have to be made about those portions of the complexes that are common to all the systems. Thus the grouping of $-C-H-Cl$ must be common to the activated complexes of all the chlorine atom reactions.

We have attempted such calculations for the reactions of chlorine atoms and methylene^{10,11}. The results obtained for the chlorine atom reactions¹⁰ are shown in Table 6. The agreement is not satisfactory presumably because the difference in the vibrational entropies of the initial and transition states is not constant for all members of the series, as was assumed.

The predictions that were made about the A factors of methylene reactions¹¹ differ even more seriously from the experimental findings. It was assumed that the activated complex closely resembled the product molecule with the rotation of the appropriate methyl group 'frozen'.

Though attempts to calculate the relative A factors of these reactions have met with little success, it is clear that the approach offers a useful way of obtaining fresh information about the activated complex. Presumably some model of the molecules can be found that will yield satis-

factory agreement. In the same way, the competitive study of reactions yields information which should be useful in a fresh approach to the more difficult problem of the calculation of energies. Perhaps the treatment of Ogg and Polanyi can be satisfactorily reduced to quantitative terms so that if the absolute activation energy of one member of the reaction series is assumed it will be possible to calculate the relative activation energies of all the other reactions.

1-Butene

1-Pentene

3-Methyl-1-butene

7.6

7.6

7.4

TABLE 1

RH	$10^{-6}k_1$ (mole ⁻¹ cm ³ sec ⁻¹)	$10^{-6}k_1/\text{active H}$ at 182°C)	E (kcal.)
Ethylene	2.9	-	10.0
Propylene	12	4	7.7
2-Butene	30	5	7.7
<u>iso</u> -Butene	26	4	7.3
2,3-Dimethyl-2-butene	76	6	7.8
1-Butene	34	17	7.6
1-Pentene	35	18	7.6
3-Methyl-1-butene	53	53	7.4
Cyclo-Pentane	11.6	4.7 (8.3)	
Toluene	11.4	6.0 (8.3)	
Acetone	11.6	6.0 (8.7)	

Table 3.

THE REACTIONS OF CHLORINE ATOMS.

RH	Log A (mole ⁻¹ cm ³ sec ⁻¹)	E (kcal)
Methane	13.4	3.9
Ethane	14.1	1.0
Propane	14.3	0.7
iso-Butane	14.3	0.9
neo-Pentane	14.1	0.7
cyclo-Pentane	14.5	0.6
Methylchloride	14.1	3.4
Ethylchloride	14.3	1.5

TABLE 4

R_1H	R_2H	A_2/A_1	(E_2-E_1)
Reactant	Product 1	per H atom	(cal.)
Methane	Ethane	2.45	-2800 \pm 30
<u>n</u> -Propane	<u>sec</u> -Propane	1.65	-445 \pm 30
<u>n</u> -iso-Butane	<u>tert</u> -iso-Butane	2.76	-340 \pm 30
<u>n</u> -Pentane	<u>n</u> -Hexane	0.7	-200 \pm 50
	2-Methyl-Pentane	1.3	-350 \pm 50
<u>iso</u> -Butane	<u>iso</u> -Pentane	1.3	-190 \pm 20

TABLE 5

THE REACTIONS OF METHYLENE FACTORS

Reactant	Product 1	Product 2	A_1 / A_2	$E_1 - E_2$ (cal.)
Propane	<u>n</u> -Butane	<u>iso</u> -Butane	1.8	-70 \pm 10
<u>n</u> -Butane	<u>n</u> -Pentane	<u>iso</u> -Pentane	0.7	-260 \pm 30
<u>n</u> -Pentane	<u>n</u> -Hexane	2-Methyl-Pentane	0.7	-200 \pm 50
	<u>n</u> -Hexane	3-Methyl-Pentane	1.3	-350 \pm 50
<u>iso</u> -Butane	<u>iso</u> -Pentane	<u>neo</u> -Pentane	1.3	-190 \pm 20
<u>n</u> -Hexane		2-Methylpentane	5.0	0.7
<u>n</u> -Hexane		3-Methylpentane	5.6	1.3

TABLE 6

CALCULATED AND EXPERIMENTAL A FACTORS

Product 1	Product 2	A_1/A_2	
The reactions of chlorine atoms.		Calc.	Expt.
Methyl chloride	Ethyl chloride	2.4	0.26
<u>na</u> Propyl chloride	<u>sec</u> -Propyl chloride	2.6	1.8
<u>iso</u> -Butyl chloride	<u>tert</u> -Butyl chloride	9.9	3.3
The reactions of methylene			
<u>n</u> -Butane	<u>iso</u> -Butane	4.3	1.8
<u>iso</u> -Pentane	<u>neo</u> -Pentane	22.2	1.3
<u>n</u> -Hexane	2-Methylpentane	5.0	0.7
<u>n</u> -Hexane	3-Methylpentane	5.6	1.3

THE REACTIONS OF METHYLENE

by J.H.Knox and A.F.Trotman-Dickenson

(Chemistry Department, Edinburgh University)

Grard and Vanpee¹ have suggested that methylene radicals add directly to alkanes in the gas phase to form higher homologues without the intervention of radicals, such as methyl, with one free valence; they did not study the systems extensively. Doering, Buttery, Lauchlin and Chauduri² have recently investigated the reactions of methylene radicals from the photolysis of diazomethane with n-pentane, 2,3-dimethylbutane and cyclopentane in solution between -80° and 30°C. They find that no cyclohexane is formed from cyclopentane and that the addition of methylene occurs with equal facility across the different types of C-H bond in the alkanes. Thus the amounts of n-hexane, 2-methylpentane and 3-methylpentane formed from n-pentane are independent of temperature and are nearly in the ratio of 3:2:1. Calculations based upon the transition state theory do not predict such a simple distribution³.

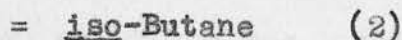
We have measured the proportions of products formed when ketene at about 5cm pressure is photolysed in a Pyrex reaction vessel in the presence of 1 to 5cm of alkane at -80° to 200°C. Negligible quantities of methane are produced. The condensable products were analysed by gas-chromatography on a 4m column of firebrick impregnated with 25% dioctyl phthalate. The expressions for the

proportions of products formed are given in the table. In some runs 30-50 cm of nitrogen was added to the reaction mixture without changing the proportions of the products.

The differences in the activation energies for attack on the various positions in the molecules are very small and hence it is likely that the overall activation energies are also small. The experimental A factors do not agree either with the predictions based on the transition state theory or with a simple statistical distribution.

The Reactions of Methylene

Typical Reactions:



Reactant	Product 1	Product 2	A_1/A_2	$E_1 - E_2$ (cal.)
Propane	<u>n</u> -Butane	<u>iso</u> -Butane	1.8	-70 \pm 10
<u>n</u> -Butane	<u>n</u> -Pentane	<u>iso</u> -Pentane	0.7	-260 \pm 30
<u>n</u> -Pentane	<u>n</u> -Hexane	2-Methyl- Pentane	0.7	-200 \pm 50
	<u>n</u> -Hexane	3-Methyl- Pentane	1.3	-350 \pm 50
<u>iso</u> -Butane	<u>iso</u> -Pentane	<u>neo</u> -Pentane	1.3	-190 \pm 20

1. Grard and Vanpee, Ann. Mines. Belg., 1950, 49, 46.
2. Doering, Buttery, lauchlin and Chaudhuri, J. Amer. Chem. Soc., 1956, 78, 3224.
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The Reactions of Methyl Radicals with Thiols

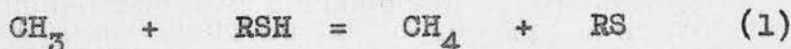
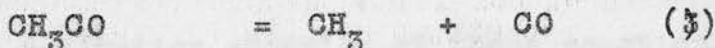
by J.A.Kerr and A.F.Trotman-Dickenson

The high reactivity of thiols with free radicals is well known; for this reason thiols are extensively used as chain-transfer agents in polymerisations. Little quantitative work on the kinetics of their reactions in solution has been reported and still less work appears to have been done in the gas phase. This note records an attempt to investigate the kinetics of the attack of methyl radicals on thiols (1).



The photolysis of acetone was used as the source of methyl radicals. In general the procedure of Trotman-Dickenson and Steacie¹ was followed. The photolysis was carried out in a Pyrex reaction vessel so that no light was absorbed by the thiols. The product gases were analysed with a standard low-temperature distillation apparatus; the carbon monoxide was oxidised in a copper oxide tube.

During the photolysis methane, ethane and carbon monoxide were produced by the following reactions:



It can be shown that:

$$\frac{k_1}{k_5^{1/2}} = \frac{R_{\text{CH}_4} - (k_4/k_5^{1/2})[\text{Acetone}] R_{\text{C}_2\text{H}_6}^{1/2}}{R_{\text{C}_2\text{H}_6}^{1/2} [\text{RSH}]}$$

where the k 's are the rate constants of the reactions and R and R are the rates of formation of the products. The application of this equation involves a knowledge of k_4 .

The value of this rate constant is uncertain at less than 100°C because methane is also formed by additional reactions, probably including the reactions of the acetyl radical². The present experiments could not be carried out at temperatures as high as 100°C because the rate of reaction (1) was so great that it was impossible to obtain reproducible results. Accordingly all the rate constants were determined at 30°C . The uncertainties in k_4 were unimportant because it is about one thousand times less than k_1 . The results obtained with the higher thiols were not very reproducible. The mean values of $10^{-7}/\text{mole}^{-1}\text{cm}^3\text{sec}^{-1}$, based on the value of k_5 advocated by Shepp³ are as follows:

MeSH	1.8	EtSH	3.5
Pr ⁱ SH	4.1	Bu ^t SH	5.9

This order of reactivity is the same as that which was deduced from a study of the photodecomposition of acetaldehyde catalysed by thiols⁴. If $\log_{10} A/\text{mole}^{-1}\text{cm}^3\text{sec}^{-1}$ for these reactions is of the order of 11.3, as it is for many reactions of methyl, then the activation energies of these reactions lie between 5.6 and 4.9 kcal./mole.

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2. Ausloos and Steacie, Canad.J.Chem., 1955,33, 47.
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4. Birrell, Smith, Trotman-Dickenson and Wilkie, in the press.